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University of Nebraska-Lincoln, tbarissov2@huskers.unl.edu

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APPLICATION OF BIOCHAR AS BENEFICIAL ADDITIVE IN CONCRETE

by

Temirlan Barissov

A THESIS

Presented to the Faculty of
The Graduate College at the University of Nebraska
In Partial Fulfillment of Requirements
For the Degree of Master of Science

Major: Civil Engineering

Under the Supervision of Professor Jiong Hu

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APPLICATION OF BIOCHAR AS BENEFICIAL ADDITIVE IN CONCRETE

Temirlan Barissov, M.S.

University of Nebraska, 2021

Advisor: Jiong Hu

Biochar is a high-carbon solid material produced via thermal decomposition of organic biomass in a low-oxygen environment. Characterized with high water retention properties and high alkalinity, biochar is generally used for soil amendment and fertilization purposes. This study is intended to explore the feasibility of using biochar as a beneficial additive of the most used manmade material, concrete.

Literature review revealed several studies where biochar was successfully implemented as an additive in concrete. The beneficial influence of biochar on the mechanical characteristics of concrete is based on nucleation and densification effects. However, the internal microstructure, porosity and chemical composition of biochar are highly dependent on the type of feedstock and production conditions. The objectives of this study do not only include the determination if a concept similar to the one described in literature (application of biochar at low dosage) could be applied by local producers, but also to explore the ways of how biochar might be used in a wider dosage and beneficially utilized in the development of environmentally and economically more sustainable materials, such as concrete mixes with reduced cement content or concrete made with recycled concrete aggregates. Several locally available biochar samples made from distillers grains, corn stover, wood waste, and red cedar were collected for characterization and incorporation in concrete mixes.

The experimental program included a study of the effect of different fineness and a wide range of biochar addition and cement replacement levels on fresh and mechanical properties of concrete, as well as the possibility of strength compensation of the concrete mixes with reduced cement content. Moreover, biochar was used as a coating for recycled concrete aggregates to improve their bonding with cement. In addition, a preliminary study of the potential use of biochar as internal curing and carbonation agent was also included. Finally, a preliminary economic analysis was performed.

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CHAPTER 1. INTRODUCTION

1.1. Background

Along with other greenhouse gases, carbon dioxide absorbs and radiates heat, released in the form of thermal infrared energy by warming up Earth's ocean and land surfaces. Not being the most harmful type of greenhouse gas in terms of the amount of heat released per molecule, carbon dioxide contributes approximately two-thirds of global warming's energy imbalance due to its relatively high concentration and long duration of stay in the atmosphere. In fact, the continuous growth of CO₂ levels in Earth's atmosphere has reached its 800,000-years peak of 409.8 parts per million (Lindsey, 2020).

According to Andrew (2018), manmade, or “anthropogenic”, carbon dioxide sources could be commonly classified as follows:

- i) Combustion of fossil fuels for energy generation
- ii) Land-use changes, such as deforestation
- iii) Decomposition of carbonates

Being a key ingredient of concrete, one of the most widely used construction materials, cement is considered to be the main source due to the decomposition of carbonates: the emitted CO₂ is originated from the chemical reaction, calcination, which implies a decomposition of raw carbonates (mainly limestone) into oxides (mainly lime) and carbon dioxide. In fact, approximately two-thirds of the total CO₂ emissions associated with cement production are attributed to calcination, while the rest third is due

to power, transportation, and other manufacture-related processes necessary for the whole process (Andrew, 2018; Czigler et al., 2020).

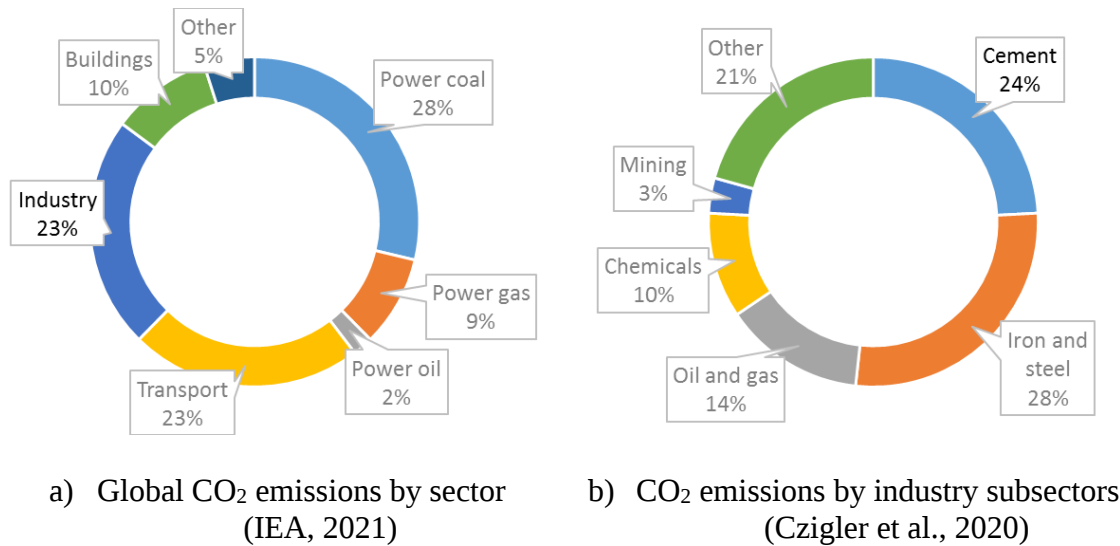


Figure 1.1. Share of global CO₂ emissions

Taking into account the fact that the industrial sector contributes about 23% of global CO₂ emissions (Figure 1.1.a), while the quarter of this could be attributed to the cement production (Figure 1.2.b), the total estimated CO₂ emissions share of the cement production is approximately 5-6%. Thus, along with other industry sectors, cement producers are starting to be forced to reduce their carbon footprint, which is hardly possible by alternating cement manufacturing and avoiding CO₂ emission during calcination, therefore leaving a more straightforward and simpler solution for the reduction of the cement consumption itself. There are currently a few alternative ways to do so, starting from the partial substitution of cement by other pozzolanic materials such as silica fume, slag, and fly ash (by-products of silicon, steel production, and coal burning), and ending up with the replacement of the concrete by more sustainable materials of construction like wood.

Another sustainable supplementary material that has recently gained attention in cement replacement is biochar, an organic material produced as a result of the pyrolysis of carbon-based biomass and organic waste (Verheijen, 2010). Although biochar is commonly used in agricultural systems as a carbon-sequestering additive, as well as to alternate soil's density, porosity, and water retention properties, this material is gaining its popularity in the production of concrete of various types, including normal, pervious, ultra-high performance and cellular concrete (Lehmann et al., 2006; Amonette & Joseph, 2012; Akhtar and Sarmah, 2018; Dixit et al., 2019; Falliano et al., 2019; Tan et al., 2021).

1.2. Research Significance

Currently, the production of biochar in North America ranges between 36,700 and 76,600 tons per year. However, the use of biochar in Nebraska and the U.S. is limited to its application in agriculture and forestry. Even though there are research works demonstrating the beneficial use of biochar in concrete, it is difficult to come up with the universal mixing design approach, as the key properties of biochar are highly variable and depend on feedstock type and production conditions.

Therefore, to ensure a successful implementation of biochar in concrete production, it is important to understand the fundamental mechanisms of influence of biochar on the basic mechanical and durability properties of concrete, as well as to understand what critical properties of biochar are more crucial to maximize its beneficial influence. It is believed that some of the locally available biochar samples might have proper characteristics to be implied in concrete. Moreover, the possibility of improving the conditions of biochar preparation (specifically post-processing and grinding) should also be attempted.

Besides following the previously proposed mixture design approaches in the attempt to incorporate a low dosage of locally available biochar in the concrete matrix to improve its mechanical and durability characteristics, this research work is intended to explore the ways biochar can be beneficially used in economical and environmentally sustainable materials development (in a much wider range of dosages):

- Concrete mixes with reduced cement content. Associated with a few benefits from materials (reduced shrinkage) and economic (reduced cost) stand points, the reduction of the cement content weakens the mechanical properties of concrete, which will be attempted to be recovered with the help of biochar.
- Concrete made with recycled concrete aggregates. Biochar is implemented to improve the bonding between the RCAs and cement paste.
- Beneficial carbonation of concrete. Internal carbonation concept might be applied for additional carbon sequestration and beneficial carbonation of concrete that may potentially increase concrete strength.

1.3. Objectives

The overall objective of this study was to demonstrate the feasibility of using locally available biochar as a beneficial additive in concrete production. Therefore, firstly, promising biochar sources were identified, and biochar samples were collected for characterization. Then, a number of different approaches of applying the selected biochar samples as beneficial additives were studied, including the application of biochar as filler, partial cement replacement, internal curing, and carbonation agent in mortar, as well as an attempt to introduce a low content of biochar to recover strength lost in mixes with reduced cement content. In addition, biochar was used to improve the mechanical

properties of concrete with recycled concrete aggregates. Finally, a preliminary cost analysis was performed to assess the economic feasibility of incorporating biochar in concrete mixes.

1.4. Thesis organization

The research study was divided into six chapters. Chapter 1 provides the general background and objectives of the study, followed by an extensive literature review, described in Chapter 2, which includes a summary of biochar production and key factors affecting the mechanisms of its influence on fresh and hardened concrete properties. Chapter 3 describes the properties of the selected raw materials, as well as concrete mixing approaches and test methods. Chapters 4 and 5 present the main experimental program, results of concrete performance and preliminary cost analysis. Finally, Chapter 6 summarizes the outputs of the whole study and includes the recommendations for future work.

CHAPTER 2. LITERATURE REVIEW

2.1. Introduction

During the last decade, in the attempt to shift to sustainable energy development and material usage, biochar has become a subject of a number of research studies aimed to introduce different concepts of beneficial biochar use in concrete. This chapter summarizes the background information of biochar production technology and its key characteristics, as well as describes the fundamental mechanisms of biochar influence on fresh and hardened concrete properties.

2.2. Production technology and key properties of biochar

Biochar is a high carbon solid substance, a product of the pyrolysis of organic matter, like wood, food waste, or animal manures, the internal structure of which is altered due to high-temperature exposure in a low oxygen environment. Besides high carbon content, the product of the pyrolysis is also characterized by an increased surface area, porous microstructure, and considerably higher resistance to degradation when compared to the source material (Major et al., 2009).

The process of biochar production is based on pyrolysis, exposure of biomass to high temperatures (generally over 400°C) in an environment of low oxygen concentration. This heating process results in a major loss of hydrogen and volatile carbon molecules, leaving a more stable mass of solid carbon, adjoin aromatic groups of molecules and some mineral ash remaining from the original feedstock (Bridgwater, 2007; Major et al., 2009).

As a result, the process leads to thermal decomposition of the original feedstock substance into syngas (can be used for power production), liquid bio-oils (production of biofuels and chemicals) and solid char, the ratio of which is dependent on pyrolysis operating conditions. Bridgwater (2012) classifies pyrolysis based on the operating temperature, residence time and the ratio of final products as follows:

Table 2.1. Classification of pyrolysis types based on process conditions and products

Pyrolysis Type	Operating Temperature	Residence time	Product Weight Percentage (%)		
			Char	Liquid	Gas
Slow Pyrolysis	300-500°C	> 10 min	35	30	35
Intermediate Pyrolysis	400-500°C	≈ 10-30 s	25	50	25
Fast Pyrolysis	400-650°C	≈ 1-5 s	12	75	13
Flash Pyrolysis	700-1000°C	< 0.5 s	10	5	85

As can be seen, associated with the highest ratio of solid char production, slow, or conventional, pyrolysis is generally considered to be an optimum technology for biochar production.

As the production of biochar implies pyrolysis of a wide range of organic matter, the original structure and composition of the source biomass are considered to be predominant factors dictating the microstructure and other physical characteristics of the final product (biochar). Although the process of pyrolysis is associated with a major mass loss and subsequent shrinkage and volume reduction, the mineral and carbon skeleton of biochar still retains the fundamental structure and porosity of the original material (Downie et al., 2012).

However, the physical properties of biochar are not solely dictated by the nature of the source biomass, but are also highly dependent on the pre-processing (e.g., drying, crushing, activation, etc.), processing (pyrolysis conditions like heating rate, temperature, residence time, etc.) and post-processing (grinding, activation, etc.) conditions.

Given the fact that the major fundamental physical changes occurring with biomass (thermal decomposition, release of volatile organics, and subsequent microstructure formation) are highly temperature-dependent, the highest treatment temperature (HTT) is generally considered to be the most influential factor amongst other pyrolysis settings like heating rate, residence time and pressure (Lua et al., 2004; Downie et al., 2012; Ghani et al., 2013). Thus, for example, a study by Lua et al. (2004) revealed an increase in surface area and enhanced pore formation of biochar samples undergoing pyrolysis at higher treatment temperatures. Attributed to a higher portion of organic volatiles to be released, it was experimentally confirmed that an increased HTT also results in higher carbon content, which may also act as an indicator of a more porous microstructure of biochar (Ghani et al., 2013; Gupta et al. 2018b).

The table below represents some of the selected examples from the research studies where biochar was used as an additive in concrete to show how the type of biomass and pyrolysis conditions affected basic properties important for its application in concrete.

Table 2.2. Effect of feedstock type and pyrolysis conditions on biochar properties

Reference	Biomass	Pyrolysis conditions	Particle size	Specific gravity	Carbon Content	Absorption Capacity
Ghani et al. 2013	Wood saw dust	550-850°C	N/A	N/A	82.3-93.4 % wt.	N/A
Khushnood et al. 2016	Hazelnut shell	850°C / 60 min	600 nm	2.20	87.7 % wt.	N/A
	Peanut shell		750 nm	2.35	93.8 % wt.	N/A
Restuccia & Ferro 2016	Hazelnut shell	800°C	N/A	N/A	97.9 % wt.	N/A
	Coffee powder		N/A	N/A	82.9 % wt.	N/A
Gupta et al. 2017	Wood saw dust	300°C / 45 min	3-200 μ m	1.54	68.3% wt.	245 %
Gupta et al. 2018a	Wood saw dust	300°C / 40 min	3-200 μ m	1.59	62.3 % wt.	735 %
		500°C / 40 min		1.51	87.1 % wt.	878 %
Akhtar and Sarmah 2018	Poultry litter	450°C / 20 min	N/A	N/A	19.0 % wt.	N/A
	Rice husk	500°C	N/A	N/A	36.1 % wt.	N/A
	Paper sludge	500°C / 20 min	N/A	N/A	30.0 % wt.	N/A
Cosentino et al. 2018	Softwood	700°C	N/A	N/A	90.2 % wt.	100 %

2.3. Mechanism of biochar influence on cement hydration and microstructure formation

The addition of various supplementary cementitious materials or other mineral powder admixtures may have a significant impact on the cement hydration kinetics.

Depending on the nature of additives, those alterations occur due to various chemical and physical phenomena (Berodier & Scrivener, 2014).

2.3.1. Influence on hydration through chemical reactions

The chemical alterations that may affect the hydration of cement are associated with a pozzolanic activity of the additives. According to ASTM C125-21 (Standard Terminology Relating to Concrete and Concrete Aggregates), the term pozzolan is referred to siliceous or siliceous and alumina-based fine material that tends to react with a water solution of calcium hydroxide to form calcium silicate hydrate. It is also worth noting that pozzolans do not chemically react with pure water.

Containing a negligible amount of silica (less than 0.5% by weight), biochar is not generally considered to fulfill a definition of pozzolanic material. However, in their study, Zeidabadi et al. (2018) achieved a high content of silica (up to 13% by weight) in rice husk and bagasse biochar through a series of pretreatment procedures implying removal of metal impurities with the help of diluted hydrochloric acid. Overall, the obtained biochar samples made from pretreated rice husk and bagasse biomass conformed to the minimum requirements for a material to be considered to have pozzolanic properties to fix 436 mg/g of calcium hydroxide (Tavares et al., 2020).

2.3.2. Influence on hydration through physical presence

As biochar is commonly considered a chemically inert additive, most of its influence on cement hydration and microstructure formation is attributed to its physical presence, or so-called filler effect, which implies three mechanisms: cement dilution, particle size distribution and nucleation effect (Lawrence et al., 2003).

The cement dilution implies the direct replacement of cement by a chemically inert additive (biochar), which consequently results in a lower amount of hydration

products. The effect of particle size distribution is attributed to the physical presence of additive particles that may occupy void spaces in between other constituents and alter the overall packing pattern of the concrete matrix. However, the relatively weak nature of biochar (in comparison to other constituents of the concrete matrix) may also influence the overall strength of the concrete. Finally, biochar may also cause heterogeneous nucleation, or seeding effect. This process implies enhanced cement hydration due to the physical nucleation of hydrates on dispersed filler particles, which subsequently accelerates the process.

Moreover, superior water absorption properties of biochar may decrease the effective water to cement ratio during the concrete mixing, leading to the decreased capillary pores formation and releasing the water for further hydration after the concrete will set, resulting in the increased mechanical strength of the concrete. In addition, a high dosage of biochar introduced in mortar tends to dramatically decrease the flowability and increase the demand for superplasticizer (Gupta et al., 2018a).

Another important factor that has a great impact on concrete mechanical and durability properties is the strength and morphology of the interfacial transition zone (ITZ), a bond between cement paste and aggregates (Scrivener et al., 2004). The strength of the ITZ is highly dependent not only on the basic morphology (shape, size, texture, roughness) but also on the porosity and water absorption and retention properties of aggregates (Vargas et al., 2017). Thus, aggregates with higher porosity may provide a better mechanical interlock between the hydration products and the pores of aggregates, as well as contribute to the increased hydration degree of the paste surrounding the aggregate by providing extra water necessary for hydration.

Similar to aggregates, this concept might be applied to biochar particles. Thus, for example, a study by Mrad and Chehab (2019) revealed a better ITZ between biochar and cement paste (in comparison to the ITZ between sand and cement paste). This was explained by denser cement paste surrounding biochar particles (attributed to the enhanced hydration due to water migration) and a better mechanical interlock of hydration products penetrating the pores of biochar.

Moreover, the biochar coating was already introduced to improve the mechanical bonding of polypropylene (PP) fibers and cement paste by Gupta et al. (2017). The study was aimed to mitigate one of the major drawbacks of PP fibers – the introduction of small air pockets that results in the increase of capillary pores and air voids. It was experimentally proven that biochar coating improved mechanical strength and lowered permeability of mortar samples due to the densification of mortar paste surrounding the fibers (as biochar tend to absorb part of mixing water and release it to promote hydration at a later age), as well as due to enhancing mechanical bonding of fibers and mortar by making the surface of PP rougher and promoting the friction.

Overall, all of the above-mentioned effects depend on:

- Biochar fineness:
 - Directly related to the particle size distribution in the concrete matrix
 - Finer particles will imply enhanced nucleation
- Biochar content:
 - A higher amount of dispersed particles increase the probability of seeding
 - A higher proportion of relatively weak biochar particles
- Biochar nature:

- Water absorption and retention properties of biochar
- The affinity of biochar microstructure to enhance water migration to improve ITZ

2.4. Influence on fresh concrete properties

Characterized by high water absorption capacity due to porous microstructure and large net surface area, depending on the amount introduced into the mix, biochar particles tend to absorb part of the mixing water, thereby decreasing the effective water to cement ratio. The decrease in the workability and/or a subsequent increase of superplasticizer demand was observed when biochar was introduced as an additive in mortar (Gupta et al., 2018a; Gupta et al., 2018b) and UHPC (Dixit et al., 2019).

Moreover, as was mentioned earlier, an introduction of fine biochar particles in concrete matrix initiates filler and nucleation effects, as well as results in the reduced amount of mixing water due to biochar's water absorption and retention properties. As fine biochar particles act as additional nucleation points, it accelerates the hydration process resulting in faster setting and increased early heat of hydration (Gupta et al., 2019b). In addition, dispersed biochar particles tend to increase the packing density of the matrix (by occupying potential void spaces between cement and sand grains), which in combination with the reduced effective water to cement ratio (due to additional water absorption by biochar), results in the increased cohesiveness and reduced potential bleeding, and thus, faster setting. The increased degree of hydration and accelerated setting was shown in the works of Gupta et al. (2018b) and Dixit et al. (2019).

2.5. Influence on mechanical properties of hardened concrete

Overall, biochar was already being widely used by a number of researchers to improve the mechanical and durability properties of not only mortar but also different types of concrete, including cellular concrete, ultra-high performance concrete (UHPC), and pervious concrete. The table below represents a selected list of previous research works to show the variety of applications of biochar in different types of concrete, where biochar was not only added as an additive but also as an actual replacement of cement or sand.

Generally, the improved mechanical strength properties of biochar-added concrete were achieved for some of the biochar dosages (the optimum dosage was individual for each study as it highly depends on biochar properties, but generally not exceeded 5%), when the positive effects of biochar addition, attributed to the decrease of effective water-to-cement ratio (due to high water retention properties of biochar), potentially improved particle packing and enhanced hydration (due to nucleation effect), overtopped the negative effects of cement dilution and low mechanical strength of biochar particles themselves (Gupta et al., 2017; Cosentino et al., 2018; Gupta et al., 2018b; Qin et al., 2021). The effect was also more apparent for the early ages and mixes with a higher water-to-cement ratio (Gupta et al., 2018a).

Table 2.3. Summary of different applications of biochar in concrete

Reference	Biomass source	Application	Biochar Dosage	Major Findings
Khushnood et al. 2016	Hazelnut & peanut shell	Additive in mortar	0.025-1% wt. of cement	- Increase of fracture energy - Improved electromagnetic shielding of concrete
Gupta et al. 2018a	Wood saw dust	Additive in mortar	1-8% wt. of cement	- Beneficial effect on strength increased with biochar carbon content; w/c ratio - Effect was more apparent for early age
Gupta et al. 2018b	Wood saw dust	Additive in mortar	2% wt. of cement	- CO ₂ treatment of biochar resulted in str. decrease
Zeidabadi et al. 2018	Rice husk & bagasse	Cement replacement in mortar	0-10% cement replacement by wt.	- Strength improvement at 5% replacement attributed to the pozzolanic activity of biochar; strength reduction at 10% - due to cement dilution
Mrad & Chehab 2019	N/A	Internal curing agent /sand replacement	0-45% sand replacement by wt.	- General drop of f'_c , which was less apparent for air-cured samples implying internal curing properties of biochar
Qin et al. 2021	Eucalyptus plywood	Cement replacement additive in pervious concrete	0-13.5% cement replacement by wt.	- Increased compressive and splitting tensile str. while keeping permeability properties of pervious concrete
Falliano et al., 2020	N/A	Additive in cellular concrete	0-4% by wt. of cement	- Decrease in compressive strength, but a slight improvement in fracture energy of air-cured samples
Dixit et al. 2019	Wood Saw Dust	Cement replacement in UHPC	0-8% cement replacement by wt.	- Effect of biochar particles size: coarser particles showed a greater strength reduction - Increased degree of hydration

It is also worthwhile to note that despite the general expectation that an increase in compressive strength should also indicate an increase in the brittleness of the material, some researchers showed that the addition of biochar resulted in the increase of fracture energy (Khushnood et al., 2016; Restuccia & Ferro, 2016; Cosentino et al., 2018). This

was explained by the fact that the mechanism of crack propagation, which is being initiated when internal stresses supply enough energy to destroy material bonds and create surface fractures, is being altered by the addition of fine particles (biochar) in the mortar matrix. Generally, any inhomogeneity of concrete matrix (like aggregates, fibers, air voids, or pores) is considered to be an obstacle for crack propagation. This requires an increase of energy needed to let the crack pass through or contour those regions, thereby leading to crack branching or deviation (Li & Maalej, 1996).

2.6. Influence on the durability of concrete

It is also important to assess the durability properties of hardened concrete, which are highly dependent on microstructure properties of concrete matrix, like pores' size and distribution, as well as their interconnectivity. Thus, for example, less durable concrete is generally characterized by a more porous microstructure with high pore connectivity, while a lower permeability of concrete is achieved by a less connected finer pore network.

The reduction of water permeability of prepared mortar samples with low biochar dosage (1-2%) was attributed to high water retention properties of biochar that resulted in the reduced amount of mixing water and subsequent densification of mortar, while samples with a higher biochar content (5-8%) showed the opposite results, implying the increased porosity due to higher ratio of porous biochar particles in mortar matrix (Gupta et al., 2018a).

Another approach to assess the durability of concrete is to assess its mass transport properties by measuring the electrical conductivity properties of concrete.

However, as the working principle of this test is based on defining the ability of concrete to resist the transfer of ions initiated by applying an outer electrical field, the results of this test are not solely influenced by pores network properties, but also by such factors as temperature, degree of concrete saturation and conductivity of pore fluid and concrete ingredients themselves (Hamed et al., 2015). Thereby, an addition of a new material (biochar) into concrete may influence the results of the concrete resistivity test not only due to an alteration of a pore network of the concrete matrix but also due to the electrical conductivity properties of the material itself.

Along with other carbon-based materials like carbon powder or graphite nanotubes, biochar was also considered as a material with high electrical conductivity properties by a number of researchers (Singh et al., 2017; Zhang et al., 2014; Jiang et al., 2013; Wang et al., 2009). Moreover, a study of Gabhi et al. (2017), as well as the work of Cantrell et al. (2012), indicated a great influence of biochar pyrolysis conditions and feedstock material on the electrical conductivity properties of biochar. Thus, a strong correlation between biochar carbon content and its electrical conductivity was experimentally confirmed.

2.7. Internal curing effect of biochar

Associated with a wide size range of pores, the microstructure of biochar is characterized by enhanced water absorption and retention capacities, which promotes its wide use in soil enhancement (Downie et al., 2012). Similar to this, these unique properties can be used to introduce a portion of the mixing water in the form of absorbed moisture by biochar particles, thereby generating an internal curing effect, the concept that is already being used in the application of lightweight aggregates (LWA) (Castro et

al., 2010). The phenomenon of internal curing is based on the enhancement of the cement hydration process, when a portion of moisture, which is lost due to external drying or internal relative humidity drop (as a result of water consumption by the hydrates chemical reaction), is being restored by the release of water that was initially pre-absorbed by porous particles, e.g. LWA (Lura et al., 2014). It is also worthwhile to note that the concept of internal curing is usually applied for mixes with either a low water-to-cement ratio (when the effect of internal relative humidity drop is significant) or for the samples undergoing poor curing (e.g., air-curing).

Moreover, as biochar particles are relatively finer and also characterized with higher water retention properties when compared to LWA, they may promote a more efficient internal curing, as the use of finer particles dispersed in the mortar matrix will result in the reduction of spacing factor (implying a shorter distance for released moisture to travel) (Castro et al., 2011).

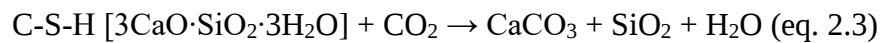
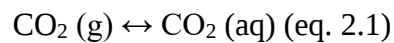
An application of biochar as an internal curing agent was already performed by several research groups. Thus, for example, Mrad & Chehab (2019) utilized a concept of a partial replacement of sand with biochar (up to 45%wt. of the initial sand content) and subjected the prepared mortar specimens to water and air curing. The results of that study revealed a significant drop in compressive strength of mortar samples with biochar addition that underwent water curing, attributed to a lower mechanical strength of biochar particles in comparison to the replaced sand. However, a significantly less strength drop was evidenced for samples under air curing, thereby confirming the potential feasibility of using biochar as an internal curing agent for the concrete samples subjected to a harsh curing environment. Another study performed by Gupta & Kua (2018) revealed an actual

strength improvement of biochar added as an internal curing additive at 2% (based on %wt. of cement) in both dry and pre-soaked conditions. The study also confirmed a more noticeable improvement in the strength of the mortar undergoing air curing. This all promotes a potential beneficial use of biochar as an internal curing agent.

2.8. Biochar for internal carbonation of cement mortar

2.8.1. Carbonation of cement mortar

The process of cement carbonation, which essentially is an absorption of the carbon dioxide and a subsequent transformation of calcium hydroxide to calcium carbonate, is generally associated with an increase in compressive and tensile strength of the concrete due to enhanced mechanical properties of calcium carbonate. However, this process can also be characterized by the volume expansion (as a result, possible microcracking of the carbonated zone), and a reduction of concrete pH (thus, reducing passive corrosion protection of the embedded reinforcement bars) (Johannesson and Utgenannt, 2001).



Nevertheless, the process starts with a dissolution of the absorbed gas molecules of carbon dioxide (eq. 1) and a formation of carbonic acid, which then reacts with calcium hydroxide (mainly) and C-S-H (at a lower rate) to finally form calcium carbonate (eq. 2 and 3). It is also worthwhile to note that the carbonation will be much less efficient

if pores of the concrete matrix will be completely occupied by water molecules (will demote the diffusion of carbon dioxide) or will be dry (not enough liquid to dissolve CO_2 and form carbonic acid) (Johannesson and Utgenannt, 2001).

Even though the process of carbonation is naturally occurring due to the presence of carbon dioxide in the air, it is being artificially utilized to benefit from enhanced mechanical properties of calcium carbonate. There might be two approaches to accelerate carbonation of concrete: external - directly exposing concrete samples to CO_2 -rich environment; or internal - incorporation of CO_2 -rich component into concrete matrix during the mixing.

2.8.2. Biochar as an internal carbonation agent

Thus, considering biochar as a material of high absorption capacity, it was supposed that biochar could be used to initiate the carbonation process from inside of the concrete matrix by introducing preliminarily treated biochar (saturated with carbon dioxide) into a mortar mix. In their study, Gupta et al. (2018b) subjected biochar to treatment in a sealed container with high CO_2 concentration and under normal pressure and temperature, and then introduced this “saturated” biochar (1.67 mmol of CO_2 per g of biochar) into a mortar mix in the amount of 2% by weight of cement. The internal carbonation was ensured by performing thermogravimetry and XRD analyses of the ground mortar samples when the amounts of calcium hydroxide and calcium carbonate (%) were estimated and compared between mortar samples. The study showed that for the given biochar dosage, a mix with CO_2 -treated biochar ended up with the highest (5.80%) amount of calcium carbonate. Interestingly, a mix with untreated biochar also resulted in increased calcium carbonate formation (3.08%) when compared with a

reference plain mortar (2.15%). This reassures the earlier emphasized hydration-enhancing properties of biochar.

The early carbonation of the cement paste may result in a reduced heat of hydration, as according to Carlson and Forbrich (1938), 1% of carbon dioxide present in a cement matrix results in carbonation and a subsequent transformation of 1.27% of calcium hydroxide to calcium carbonate, given that heat of solution of calcium carbonate (102 cal. per gram) is considerably less than of calcium hydroxide (557 cal. per gram). This was also experimentally confirmed by Gupta et al. (2018b) when a mortar mix with CO₂-treated biochar added resulted in a generated heat of hydration significantly lower than of the mix with untreated biochar.

However, in the same study, mortar samples with CO₂-treated biochar added showed the lowest compressive and tensile strength characteristics when compared with the reference plain mortar and the mix with untreated biochar. This was attributed to a possible microcracking and debonding due to volume expansion as a result of carbonation chemical reactions (Gupta et al., 2018b). A similar result of the strength drop due to the addition of CO₂-treated biochar was shown in the study of Wang et al. (2020), when 1% of pre-treated biochar (treated at 16 psi CO₂ pressure for 24 hours) was added to the mortar mix. However, no sign of additional carbonation was revealed as a result of the conducted thermogravimetric analysis (TGA).

Interestingly, the same research group (Wang et al., 2018) introduced a concept of external carbonation of biochar-added mortar samples, which were subjected to the same CO₂ treatment conditions upon the completion of the demolding process (16 psi for 24 hours). This time, the TGA of the CO₂-treated mortar blocks revealed a decrease of CH

content by 21% (transferred to C-S-H and CC), which led to an increase of compressive strength by 68%.

2.8.3. Type of the adsorption mechanisms and factors affecting them

According to Fang (1997), adsorption can be defined as the process of inter-molecular penetration of materials of two different phases (in this case – carbon dioxide and biochar). Based on its nature, this process can be divided into physical (van der Waals) or chemical (activated) adsorption. In the process of physical adsorption, molecules are being held by means of intermolecular attraction - van der Waals forces. The process is also generally characterized by low heat of absorption and weak binding energy in the levels not sufficient to result in any chemical changes. It is commonly suggested that the process of CO₂ absorption by biochar particles follows van der Waals (physical) adsorption and is essentially exothermic (Creamer et al., 2014; Bamdad et al., 2019).

Generally, an adsorption capacity might be affected by a number of factors such as pressure, temperature, and the nature of the adsorbent. Thus, it was theoretically proposed by Fang (1997) and experimentally confirmed by Creamer et al. (2014) that the efficiency of the CO₂ absorption might be increased due to an increase in pressure. Moreover, suggesting that the carbon dioxide captured by biochar is exothermic in nature, reducing the temperature of the process is another factor in enhancing the process (Creamer et al., 2014; Bamdad et al., 2019).

In addition to this, Dissanayake et al. (2020) suggest that the specific surface area, as well as the size of the pores, are the essential characteristics of biochar that influence

its absorption capacity. This was also experimentally confirmed by Ghani et al. (2013), Lahijani et al. (2018), and Bamdad et al. (2019), in studies of whom biochar samples that were prepared under higher pyrolysis temperature (suggesting that an increase in pyrolysis temperature generally results in the increase of the pore size) demonstrated higher absorption capacity.

Another important factor that could influence the adsorption of CO₂ is the alkalinity of the adsorbent (biochar). Lahijani et al. (2018) theoretically suggested that an increase of the biochar surface alkalinity may promote the absorption of acidic CO₂ gas molecules, and, moreover, experimentally confirmed that CO₂ adsorption by biochar could be enhanced by the introduction of Mg, Al, Fe, Ni, Ca or Na (ions of the basic metal group) onto the biochar surfaces. A similar positive correlation of CO₂ absorption and biochar alkalinity was shown in the study of Dissanayake et al. (2020).

Several research groups utilized thermogravimetric analysis to study the process of the CO₂ capture by biochar and summarized the process as rapid in the beginning, followed by a reduction of the rate of the absorption after approximately 10 minutes, and finally approaching the equilibrium close to 1 hour time mark (Creamer et al., 2014; Lahijani et al., 2018).

Moreover, a similar thermogravimetric study of carbon dioxide absorption and subsequent desorption performed by Ghani et al. (2013) proposed that depending on their size and absorption mechanism, micropores of the biochar may be divided into three groups. The first and the most predominant group – micropores of the size much larger than the CO₂ molecule, which suggests immediate adsorption and subsequent rapid desorption of captured carbon dioxide molecules. The second group is attributed to slow

absorption and desorption, which require heating. The micropores of the third group are considered to capture and almost not release the CO₂ molecules.

Overall, this study will imply both external carbonation of fresh mortar cubes by directly introducing them in a CO₂-rich environment and internal carbonation of mortar through the introduction of preliminarily treated biochar particles into the fresh concrete matrix.

2.9. Summary

The conducted literature review introduced a summary of biochar production technology and the key properties of the material, which then helped to understand the fundamental mechanisms of influence of biochar on concrete fresh and hardened properties. Biochar is generally considered as a non-pozzolanic additive, which interferes with cement hydration and concrete matrix formation through its physical presence, the effect of which is highly dependent on the nature of the feedstock biomass, its porous microstructure, and particles size. However, a rough estimation of which factor has a more crucial effect on mechanical and durability properties of concrete may be helpful for initiating the process of establishing specifications and promoting biochar application in concrete mixing.

Among the positive effects of biochar implication, the following ones can be highlighted: enhanced cement hydration due to nucleation effect, mortar strengthening as a result of the reduction in the effective water to cement ratio due to high water absorption properties of biochar, which also imply the internal curing effect. On the other hand, the introduction of biochar may also result in the drop of workability and the

decrease of the concrete mechanical properties due to the reduction of cement content (cement replacement with chemically inert biochar) and the porous and weak nature of the particles themselves.

Overall, different biochar application approaches conducted by other researchers were reviewed. Despite the differences in the biochar incorporation approaches and the fact that the results of each individual study were highly dependent on the biochar sample used in the study, in general, a positive effect of a low optimum dosage of biochar was confirmed by a number of studies.

As there was no uniformity in the mixing designs and approaches, as biochar was added as an additive, as well as a partial replacement of cement or sand, it was decided to not only follow the most common approach of the addition of biochar at a low dosage of addition or cement replacement (without any adjustments in the mix design) but also to explore a wider range of biochar content application, as well as an attempt to improve its beneficial use through post-processing (grinding and carbonation). Moreover, it was decided to explore other approaches, beneficial in the way to not necessarily improve concrete strength properties, but to promote the application of biochar in more economic and environmentally sustainable materials with comparable concrete mechanical characteristics, such as mixes with significant reduction of cement content or concrete made with recycled concrete aggregates.

CHAPTER 3. MATERIALS AND TEST METHODS

This section describes materials used in the study, as well as test methods included in the experimental program, which consisted of biochar characterization and post-processing (grinding), mortar and concrete mixing and testing, treatment of biochar, and mortar samples with CO₂.

3.1. Materials

3.1.1. Cement and cementitious materials

Type IP Portland-pozzolan interground and blended cement containing 25% of Class F fly ash and conforming to ASTM C595 (Standard Specification for Blended Hydraulic Cement) was selected and used as the main cementitious material used for cement mortar mixing.

Type I/II Portland cement meeting the requirements of ASTM C150 (Standard Specification for Portland Cement) was used for preparing concrete specimens.

Table 3.1. Chemical composition and physical properties of cement types

Type	Property/Content	Type I/II	Type IP
Physical Properties	Specific Gravity	3.15	2.95
	Blaine Fineness, cm ² /g	4000	4400
Chemical Composition	MgO, %	2.30	2.45
	SO ₃ , %	2.70	3.10
	Loss on Ignition, %	-	1.00
	Pozzolan Content, %	-	25

3.1.2. Aggregates

Locally available river sand (Omaha, Nebraska) was used as the base fine aggregate in mortar and concrete mixes preparation. Additionally, a sample of recycled

concrete aggregates (RCA) collected from highway demolition (North Carolina) was used as a base coarse aggregate constituent of concrete mixes.

To compare the internal curing properties of the biochar, a sample of expanded clay (Boulder, CO) that can be classified as a lightweight fine aggregate (LWFA) due to its low specific gravity and high water absorption capacity was introduced to this study and used for the partial/full replacement of the river sand in mortar mixes.

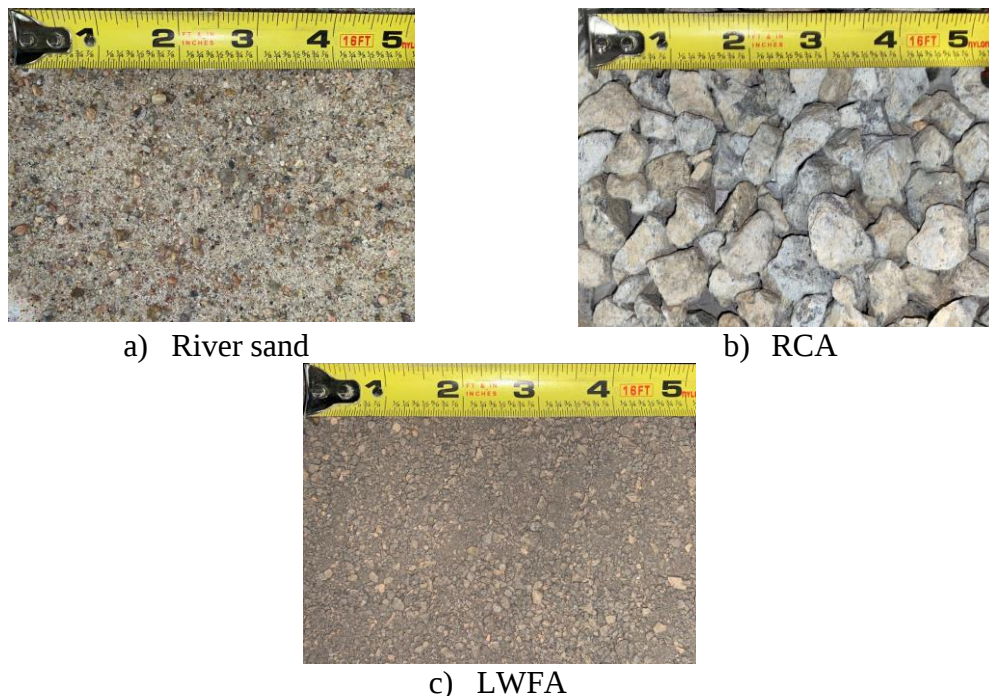


Figure 3.1. Aggregates selected for this study

The basic physical properties like specific gravity and water absorption (measured conforming ASTM C128 (Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Fine Aggregate), ASTM C127 (Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Coarse Aggregate), and ASTM C1761 (Standard Specification for Lightweight Aggregate for Internal Curing of Concrete) for river sand, RCA and LWFA accordingly), as well as their gradation (by

means of ASTM C136 (Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates)), are demonstrated in the following table and figure:

Table 3.2. Physical properties of aggregates used in the study

Aggregate	Source	G _{sb, SSD}	Water absorption (%)
River sand	Omaha, NE	2.65	0.52
LWFA	Boulder, CO	1.91	22.4
RCA	NC	2.40	6.05

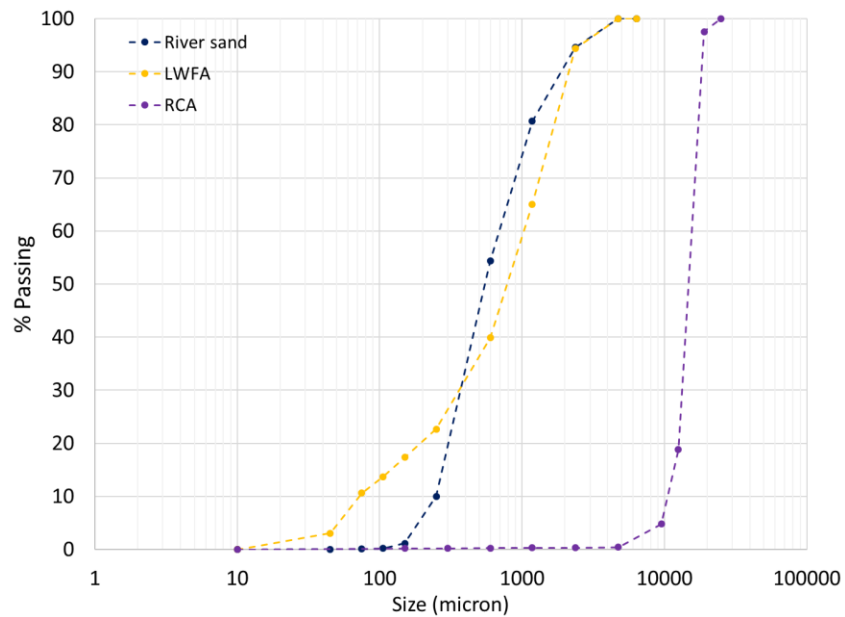


Figure 3.2. Gradation curve of aggregates used in this study

3.1.3. Chemical admixtures

A polycarboxylate full-range water-reducing admixture, MasterGlenium 7500, and mid-range water-reducing admixture, EUCON X15, both conforming to ASTM C494 (Standard Specification for Chemical Admixtures for Concrete) were used to enhance the workability of fresh cement mortar and concrete accordingly.

Table 3.3. Physical properties and recommended dosage of admixtures

Admixture	Type	Specific gravity	Recommended dosage	Application
MasterGlenium 7500	Superplasticizer (SP)	1.05	2-15 fl.oz/cwt	Mortar mixing
EUCON X15	Water-reducer (WR)	1.27	4-15 fl.oz/cwt	Concrete mixing

3.1.4. Biochar

Several samples of biochar of different feedstock types and produced under different pyrolysis conditions were collected from local producers (Figure 3.3) and listed in the following table:

Table 3.4. List of the collected biochar samples

Biochar ID	Supplier	Location	Material Type
B1	Barcel Mill & Lumber	Bellwood, NE	Distillers Grain
B2	Frontline/NPPD	Nevada, IA	Corn Stover
B3	Barcel Mill & Lumber	Bellwood, NE	Wood waste (pallets, crates, plywood, C&D materials)
B4	Frontline/NPPD	Nevada, IA	Red cedar



a) B1



b) B2



c) B3



d) B4

Figure 3.3. Biochar samples collected for the study

The particle size distribution of received biochar samples was measured by means of standard sieve analysis following ASTM C136 (for coarse B3 biochar sample) and a wet method of laser particle size determination using the Microtrac S3500 laser particle size analyzer (for the remaining B1, B2, and B4 samples). As can be seen from figure 3.4, biochar samples B1 and B3 were of the size comparable to fine aggregates, while B2 and B4 were finer but still a little coarser than cement particles. It is also worthwhile to note that B3 sample appeared to be the most inhomogeneous as it contained a number of elongated particles.

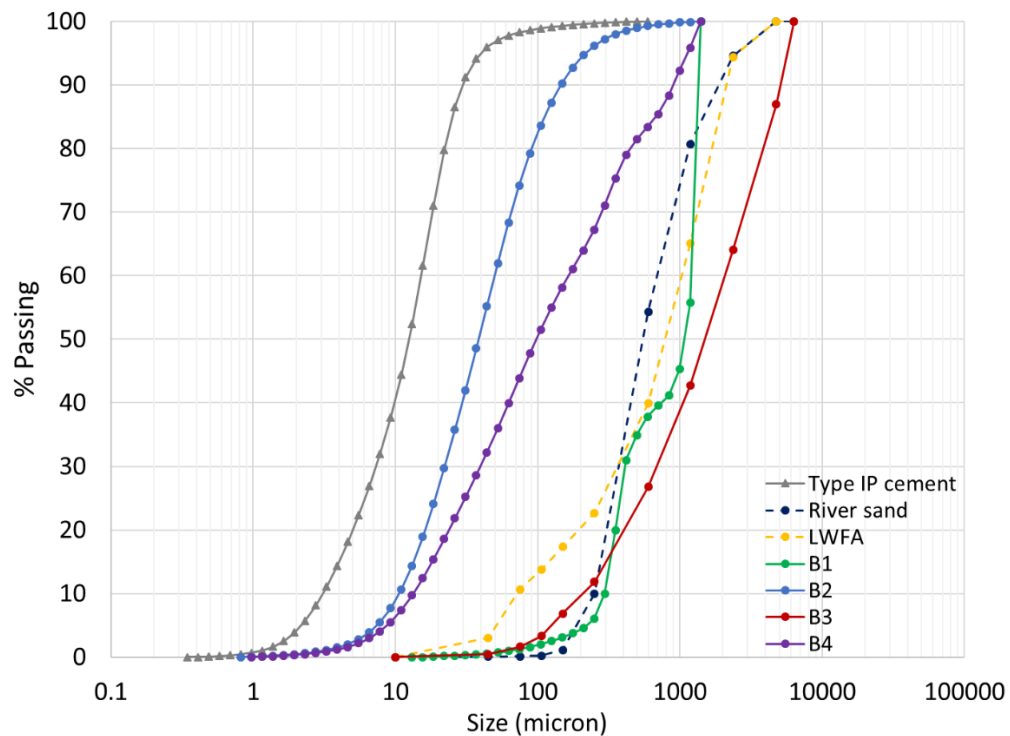


Figure 3.4. Particle size distribution of collected biochar samples in comparison with cement and fine aggregates.

The carbon content of biochar was measured with the help of the ELTRA CS-200 analyzer, as well as the rest chemical composition was identified by means of X-ray fluorescence (XRF) analysis of a pressed powder pill. As can be seen from Table 3.5, almost all the biochar samples ended up containing a similar content of carbon (around

72-78%) in the range comparable to biochar samples previously used by other researchers (Table 2.2), except for the corn stover biochar sample, which was characterized with the lowest carbon content of 32.93% and the highest silica content, which can potentially indicate a pozzolanic activity of this particular biochar sample, similar to what was shown by Zeidabadi et al. (2018) (section 2.4.1).

Table 3.5. Chemical composition of the collected biochar samples

Oxide/Element	Distillers grain biochar B1	Corn Stover Biochar B2	Diverted Wood Waste B3	Red Cedar Biochar B4
SiO ₂	1.89	25.62	3.60	2.53
Al ₂ O ₃	0.58	1.33	0.41	0.29
Fe ₂ O ₃	8.07	2.06	2.49	0.73
CaO	1.45	14.39	9.58	20.57
MgO	0.51	0.36	0.31	0.14
SO ₃	0.49	0.52	0.34	0.08
Na ₂ O	0.02	0.05	0.08	0.02
K ₂ O	4.22	19.52	3.72	2.43
TiO ₂	1.77	0.28	0.14	0.08
P ₂ O ₅	7.23	1.24	0.67	0.67
Mn ₂ O ₃	0.07	0.26	0.49	0.25
SrO	0.00	0.06	0.06	0.08
ZnO	0.15	0.03	0.07	0.01
Cr ₂ O ₃	0.09	0.06	-	-
CuO	0.13	0.03	0.10	-
BaO	-	0.07	-	0.05
Gd ₂ O ₃	-	0.07	-	-
NiO	0.04	-	-	-
ZrO ₂	-	0.05	0.03	0.02
Cl ⁻	0.03	1.13	0.21	0.10
C*	73.25	32.93	77.69	71.95
Total	99.98	99.96	99.98	100.00

*Measured with Eltra Analyzer; remaining – via XRF analysis

3.2. Aggregates and biochar characterization test methods

The following section will describe test methods used to measure the main physical and chemical properties of aggregate and biochar samples.

3.2.1. Sieve Analysis

The gradation of the aggregates and coarse as-received biochar samples (B1 and B3) was identified following ASTM C136 (Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates), where biochar was treated in the same manner as a sample of fine aggregate. However, due to its lower specific gravity, the test sample size of biochar was reduced from the required minimum of 300g (for fine aggregates) to 100g of biochar. A sample of the test material was then dried to a constant mass at $110\pm5^{\circ}\text{C}$ and subject to sieve analysis using a mechanical sieve shaker presented in Figure 3.5.

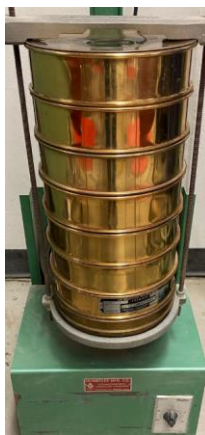


Figure 3.5. Set of sieves and a mechanical shaker

3.2.2. Standard test method for relative density (specific gravity) and absorption of fine aggregate

The specific gravity and absorption capacity of the biochar samples were measured by means of ASTM C128 (Standard Test Method for Relative Density

(Specific Gravity) and Absorption of Fine Aggregate). A representable sample of the biochar was soaked in water for 72 ± 4 h and was stirred for 1 min every 24 h, as specified for lightweight aggregates. The excess water was then drained off and the biochar sample was subjected to a gentle airflow using a regular hairdryer (Figure 3.6.a) until the saturated surface dry (SSD) condition was achieved, which was checked using a cone mold (Figure 3.6.b). The specific gravity and absorption capacity were then checked by the gravimetric method with the slight change of the required amount of the SSD sample from 500 g (for normal fine aggregate) to approximately 100 g of biochar (due to its lower bulk density).



a) Drying wet biochar samples using a hairdryer



b) Checking the moisture condition using a cone mold and a tamper

Figure 3.6. Preparation of the SSD biochar for measuring Specific Gravity and Absorption Capacity by ASTM C128

Despite its simplicity, the test revealed several disadvantages, such as increased test run-time and the loss of airborne particles even at a low-speed stream of air (due to low specific gravity). Thereby, it was decided to apply the following alternative method to measure the above-mentioned properties. It is also worthwhile to note that this test method was only applicable for testing B1 (distillers grain) biochar, as other samples were not very homogenous (B3) or contained a significant amount of fine particles

making it even impossible to use a hairdryer due to formation of airborne particles (B2 and B4).

3.2.3. Standard test method for relative density (specific gravity) and absorption of lightweight aggregate

To compensate above-mentioned drawbacks of application of the ASTM C128, it was decided to further imply the concept of absorption and relative density testing methods described in ASTM C1761 (Standard Specification for Lightweight Aggregate for Internal Curing of Concrete), which differs from ASTM C128 in terms of the way of achieving and controlling the moisture condition of the sample. In this method, it is recommended to use paper towels to absorb and remove any free moisture (Figure 3.7.a-b) until the surface of paper towels appears dry and free of any free water (Figure 3.7.c). The rest of the test was similar to ASTM C128. However, this test method was also applicable for testing only the B1 biochar sample, as the fine biochar portion of particles from the remaining biochar samples tended to adhere to paper towels.



a) Wet biochar sample placed on several layers of paper towel

b) Wet paper towel (beginning of the drying procedure)

c) Almost dry paper towel (near to the end of the drying procedure)

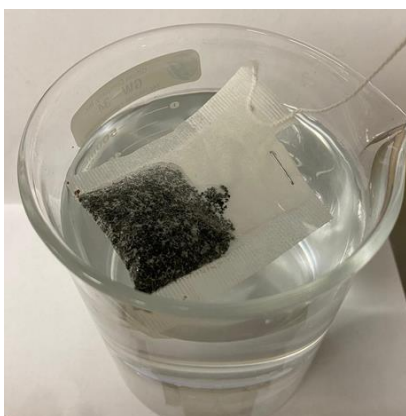
Figure 3.7. Preparation of the SSD biochar for measuring Specific Gravity and Absorption Capacity by ASTM C1761

3.2.4. Teabag method for absorption capacity/rate measurement

A method initially introduced by Schrofl et al. (2012) for measuring the water absorption properties of superabsorbent polymers was implied to measure similar characteristics of the biochar. Approximately 1.5 grams of oven-dry biochar were placed in an ordinary teabag (of known mass and absorption capacity) and immersed in water to check the amount of water that will be absorbed by the biochar particles after the 30s, 2 min, 5 min, 10 min, 15 min, 15 min, 30 min, 1 h, 24, 48 h and 72 h. The SSD moisture condition of both teabag and inside biochar was achieved using paper towels. It is also worth noting that teabags were not squeezed to avoid damage to brittle biochar particles, thus it is possible that some amount of the excess water might still be entrapped between particles. However, a comparison between the results obtained by the teabag method and microscopy showed no significant difference (Farzanian et al., 2016). Nevertheless, this test method was also only applicable for B1, as the fine biochar portion of particles from the remaining biochar samples tended to escape the mesh of a teabag.



a) Dry teabag filled with dry biochar



b) Teabag immersed in water



c) Teabag and biochar - dried using paper towels

Figure 3.8. Teabag method setup and procedure

3.2.5. Water desorption properties

ASTM C1761 also describes a procedure for measuring the desorption of lightweight aggregates, which was implied to test the ability of the initially SSD biochar to release absorbed water at 94% relative humidity and $23.0 \pm 1^\circ\text{C}$ temperature condition. For this test, approximately 5 grams of SSD biochar (prepared following previously mentioned ASTM C1761 “paper towel” method) were placed in an environmental chamber, a sealed plastic container with 300g of supersaturated solution of potassium nitrate (figure 3.9). A mass of the sample was then measured every 24 hours until no difference (to the nearest 0.01 g) was noticed.

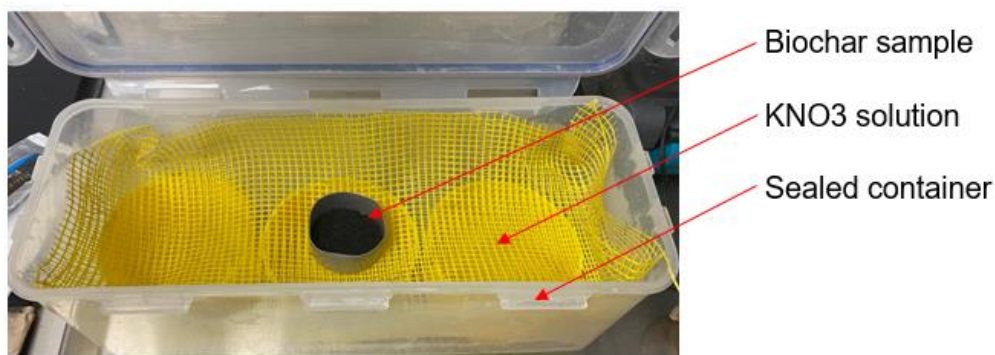


Figure 3.9. Setup for the desorption measurement by ASTM C1761

3.2.6. Biochar grinding procedure

Grinding of the original biochar sample was performed in two ways. At first, using a jar mill in the following manner: 150 ml of original bulk material (in the oven-dry state) were ground for 20/120 minutes (depending on the desired fineness level G1/G2 respectively) at 100 rpm and using a charge of 20 ceramic cylinders (Figure 3.10.a). The amount of biochar was chosen so that the jar will not be filled for more than 25-30% of the total volume, thereby providing sufficient space for material and charge to proper mix and grind inside of the container.

The second approach was performed as an attempt to replicate a jar mill approach but on a large scale for the samples when more biochar material was available. For this approach, 3 kg of the original oven-dry biochar sample were loaded in the LA Abrasion machine (Figure 3.10.b) and subjected to 2000/4000 rotations under a charge of 12 standard steel balls.



a) Jar mill



b) LA Abrasion machine

Figure 3.10. Biochar grinding setup**Table 3.6.** Summary of biochar grinding procedure

Biochar ID	Original sample	Grinding setup	Grinding level (rotations)
B1G1	B1	Jar mill	2000 (at 100rpm)
B2G1	B2	Jar mill	2000 (at 100rpm)
B2G2	B2	Jar mill	12000 (at 100rpm)
B3G1	B3	LA Abrasion machine	2000 (at 30rpm)
B3G2	B3	LA Abrasion machine	4000 (at 30rpm)
B4G1	B4	LA Abrasion machine	2000 (at 30rpm)

The overall objective of this procedure was to grind the original biochar into the powder-like fine form of particle sizes comparable to cement grains or biochar samples used previously by other researchers (Section 2.3: Table 2.2). As can be seen from the

particle size distribution of ground biochar samples (Figure 3.11), the desired fineness of biochar was generally achieved (below 200 microns), with the B2G2 sample almost reaching the fineness level of Type IP cement particles. Although, no recommendation of grinding setup and duration might be made due to the fact that the efficiency of the procedure depends on biochar material type (microstructure) and original fineness.

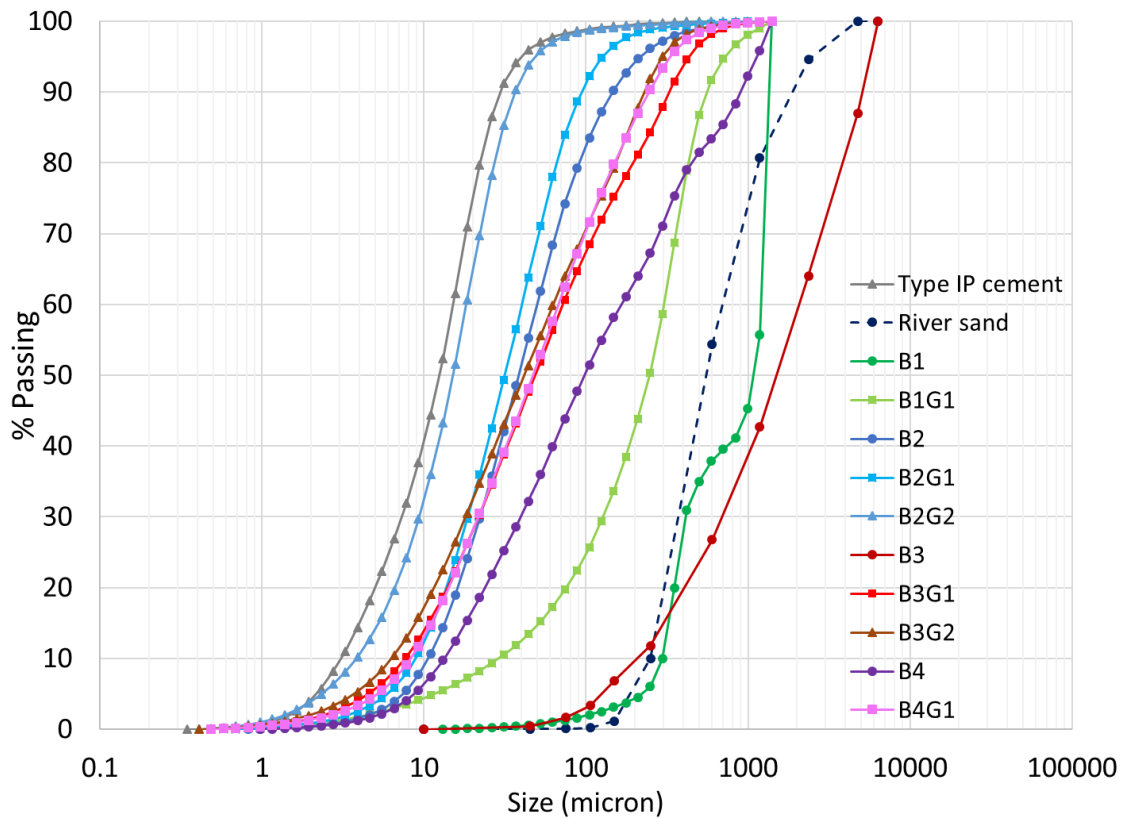


Figure 3.11. Particle size distribution of the ground biochar samples

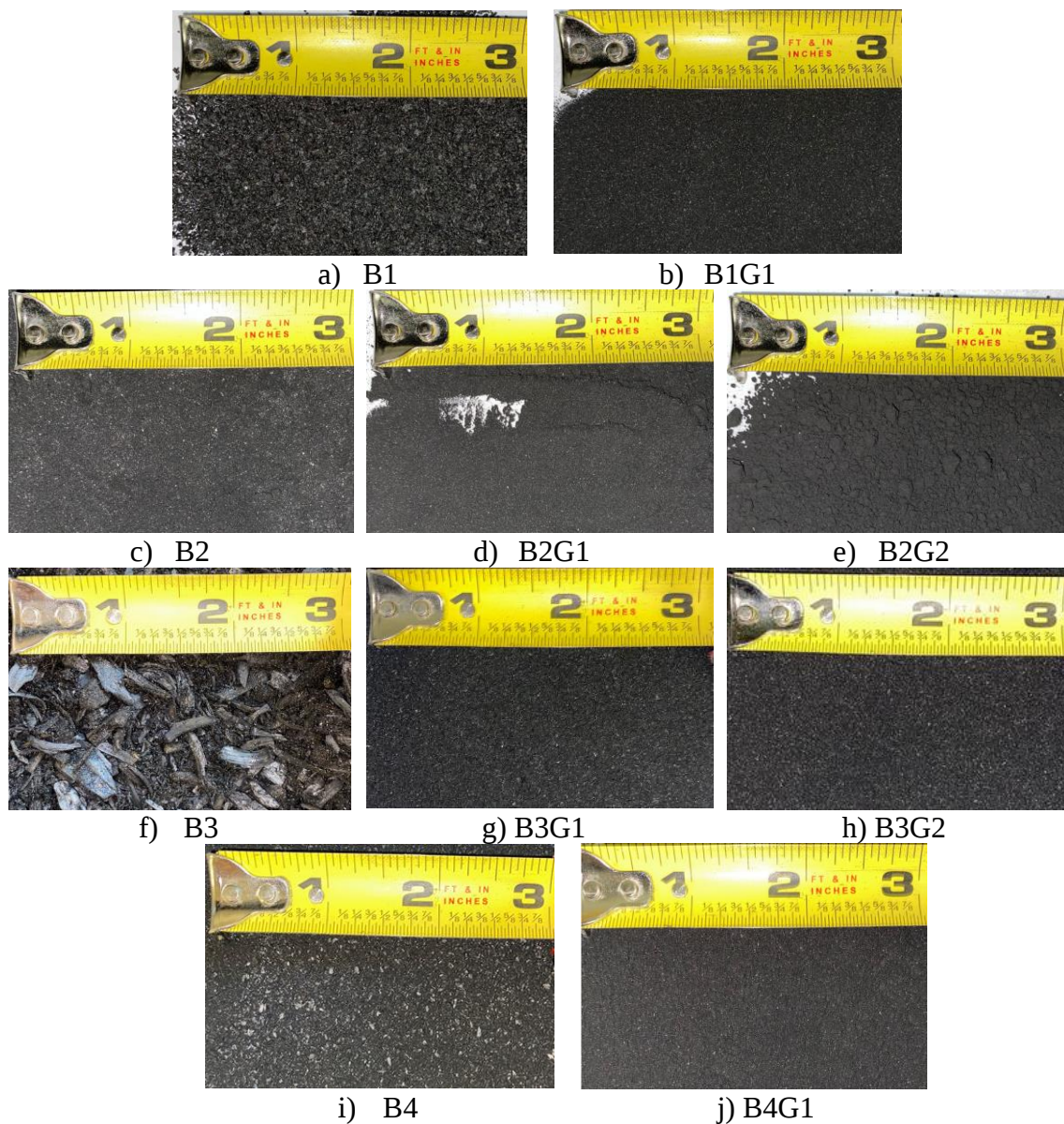


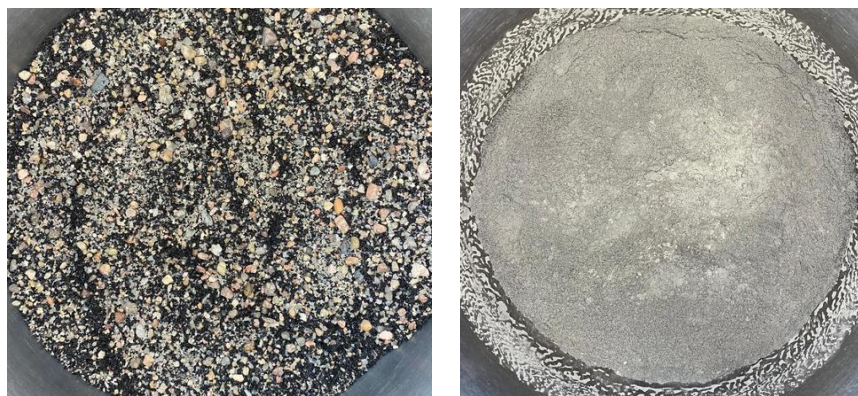
Figure 3.12. Comparison of original and ground biochar samples

3.3. Concrete mixing, casting and curing

3.3.1. Mortar mixing

A set of hydraulic cement mortar mixes with the reference mix conforming to 0.43 water-to-cement, and 2.75 sand-to-cement ratios were prepared. The water-to-cement ratio of 0.43 was selected to obtain a flow of $110 \pm 5\%$ for the reference mix, following the requirement dictated by ASTM C109 (Standard Test Method for Compressive Strength of Hydraulic Cement Mortars).

Similar to the mixing approaches utilized by previous researchers (described in chapter 2), implying a premix of biochar with either dry components of the mix or sonicating it in mixing water for better dispersion and avoiding a possible clumps formation, it was decided to pre-mix oven-dry biochar with either sand or cement in a mixer for 30 s with the subsequent addition of the premixed substance into the mix in the order when the main component was supposed to be added (Figure 3.13). The exact method of biochar implication, as well as mix proportioning, are to be described in detail in subsections 4.1-4.5.



a) B1 premixed with sand b) B1G1 premixed with cement

Figure 3.13. Examples of biochar premixing

However, for the part of the study intended to explore internal curing properties of biochar and LWFA, where the amount of the internal curing agent is identified based on its water absorption/desorption properties as was initially introduced by Bentz & Snyder (1999) and then modified by Castro (2011):

$$M = \frac{C_f \times CS \times \alpha_{max}}{t^A \times \phi_{24} \times \psi} \quad (\text{eq. 3.1})$$

M – dry mass of the biochar/LWFA (pcy)

C_f – amount of the cement in the mix (pcy)

CS – chemical shrinkage of the cement (for Type IP = 0.1011 as per Wang et al., 2013)

α_{max} – degree of cement hydration (expected to be 1.0 for w/c ratio of 0.43)

t^A – time-dependent coefficient of the water absorption (1.0)

ϕ_{24} – 24h water absorption of the biochar/LWFA

ψ – desorption coefficient (measured as described in 3.2.4)

This method also implies the use of the biochar/LWFA in pre-soaked condition. The method of materials preparation was adapted from Abdigaliyev et al. (2020), when the material (initially oven-dried at $110 \pm 5^\circ\text{C}$ and cooled down to normal room temperature) was batched at the amount calculated based on equation 3.1 and placed in the plastic container filled with water. The plastic container (4×6” cylinder) had nine 1/16” pre-drilled openings evenly distributed throughout the bottom of the container and initially taped to avoid water loss (Figure 3.14). After the 24-hour period of soaking in water, the openings were released, thereby letting the extra water drain from them for approximately 1-1.5 hours. The mass difference of the material before and after soaking indicated the moisture content of the material, which then was used to adjust the actual required batch size of the water. The pre-soaked biochar/LWFA was then introduced to the mix with the sand.



Figure 3.14. The bottom of the plastic cylinder for biochar/LWFA saturation

After that, regardless of the pre-mixing approach of biochar with cement or sand, a standard ASTM C305 practice for hydraulic cement mortar mixing was followed using Hobart N50A 5 qt planetary mixer, when cement (or cement premixed with biochar) is added to water and mixed at slow speed for 30 s, followed by the addition of the sand (or premixed sand and biochar) over next 30 s, after which the mixing speed is changed to medium and run for another 30s. Then, the mortar is left to rest for 90 s, followed by 60 s of final mixing at medium speed. When the flow table test is performed or the water reduced is applied, the mortar is being additionally mixed for 15 or 30 seconds, respectively.

Once the mixing procedure was completed, mortar specimens were cast following ASTM C109 and kept in a $73.5 \pm 5.5^\circ\text{F}$ ($23.0 \pm 3.0^\circ\text{C}$) room for 24 hours, after which being demolded and placed in lime-saturated water for curing.

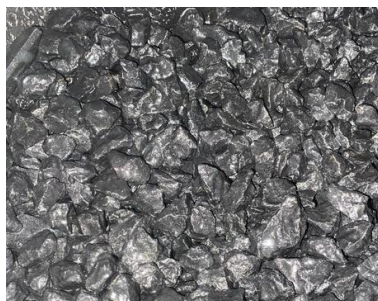
3.3.2. Concrete mixing

A set of concrete mixes was prepared using a drum mixer of a 0.3-ft^3 capacity by first introducing biochar in the mix (described in Table 3.7 and shown in Figure 3.15), and then following a standard mixing procedure described in ASTM C192 (Standard

Practice for Making and Curing Test Specimens in the Laboratory). It was attempted to improve the ITZ between aggregate and cement paste by covering RCA particles with biochar or biochar-rich paste:

Table 3.7. Steps of biochar addition

Biochar addition approach A	Biochar addition approach B
- Introduce RCA and 30% of mixing water – mix for 30 sec - Add biochar while the mixer is running – 30 sec - Follow the remaining steps as per ASTM C192	- Premix biochar with 25% of cement paste in a planetary mixer - Add the prepared biochar paste into the mixer with RCA – mix for 30 sec - Follow the remaining steps as per ASTM C192



a) Approach A



b) Approach B

Figure 3.15. RCA covered with biochar/biochar-rich paste

After RCAs were covered with biochar/biochar-rich-paste, sand, cement, and the remaining portion of mixing water were introduced into the mixer. The mixer then was kept rotating for 3 minutes, proceeded with a 3-minutes resting period, and finished with two more minutes of mixing. In case when it was required to add a water-reducing admixture (WR) to adjust workability (presumably reduced due to biochar's high water retention properties), the WR was introduced in a rotating mixer and kept running for additional 3 minutes.

Concrete specimens then were cast, demolded (after keeping them undisturbed for 24 hours at $73.5 \pm 5.5^\circ\text{F}$ ($23.0 \pm 3.0^\circ\text{C}$)) and subjected to moist curing in an environmental room with 100% RH.

3.4. Fresh Concrete Properties

3.4.1. Flow Table Test

The flow of each mortar mix was assessed according to ASTM C1437 (Standard Test Method for Flow of Hydraulic Cement Mortar): a specified conical mold was placed on a flow table and filled with fresh cement mortar and removed, followed by 25 drops of flow table within 15s (Figure 3.16). The final value of the resultant diameter was calculated as an average of four measurements along scribed lines on the surface of the flow table. The flow is then represented by the percentage increase of the original base diameter.



Figure 3.16. Flow table assembly

3.4.2. Heat of hydration and setting time

Mortar hydration was assessed by measuring the heat of hydration following ASTM C1702 (Standard Test Method for Measurement of Heat of Hydration of Hydraulic Cementitious Materials Using Isothermal Conduction Calorimetry). The

amount of heat released from the mortar sample was captured by heat-flow sensors in the isothermal calorimeter (Figure 3.17). The data captured by the equipment was used to estimate the total heat of hydration (generated by the mortar sample during the first 72 hours of hydration) and initial and final setting time values following the approach described by Hu et al. (2014).

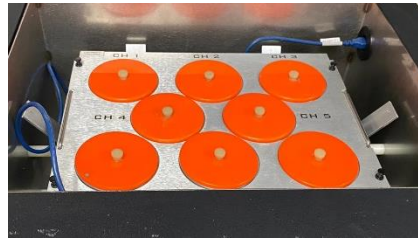


Figure 3.17. Isothermal calorimeter

3.4.3. Slump test

The workability of concrete was assessed by means of ASTM C143 (Standard Test Method for Slump of Hydraulic-Cement Concrete), which was performed within 2.5 minutes upon finishing the mixing procedure.



Figure 3.18. Slump test setup

3.5. Hardened Concrete Properties

3.5.1. Compressive strength

The compressive strength of hardened cement mortar was measured employing ASTM C109 (Standard Test Method for Compressive Strength of Hydraulic Cement Mortars). Three cubic specimens (2 in $\times$ 2 in $\times$ 2 in) were subjected to compression using a Forney compression testing machine (at a rate of 200-400 lb/s) at 1, 3, 7, 28, and 90 days of age.

The compressive strength of hardened concrete samples was measured in accordance with ASTM C39 (Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens). The test was performed by subjecting hardened cylindrical specimens (3 in $\times$ 6 in) to loading at 35 ± 7 psi/s using a Forney compression testing machine at 7 and 28 days of age.



Figure 3.19. Compressive strength testing apparatus

3.5.2. Splitting tensile strength and ITZ examination

A splitting tensile strength of hardened concrete specimens was measured with accordance to ASTM C496 (Standard Test Method for Splitting Tensile Strength of Cylindrical Concrete Specimens) when 28-days cured concrete cylinders (4 in × 8 in) were subjected to a splitting loading at a 2.5 ± 0.8 psi/s rate (figure 3.20).



Figure 3.20. Splitting tensile strength testing apparatus

Moreover, a crack propagation pattern that could be observed on the inner cross-section surface of the sample after splitting tensile strength test can possibly be used to quantify the strength of aggregate-cement paste bonding in the following manner:

$$P = \frac{A}{A + Z} \times 100\% \text{ (eq. 3.2)}$$

P - percentage of cracks propagated through aggregates

A – number of broken aggregates*

Z – number of broken ITZs*

The number of broken aggregates and ITZs are being manually counted on each surface of the exposed cross-section of a broken concrete cylinder (Figure 3.21). Then, the average of the two samples was calculated.

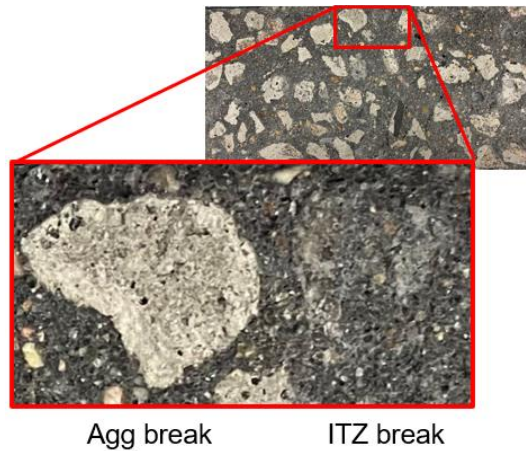


Figure 3.21. Examples of aggregate and ITZ breaks

3.5.3. Mortar shrinkage (Volume stability)

The volume stability of the mortar specimens was evaluated by monitoring the change in length of the concrete samples under two different curing and exposure conditions.

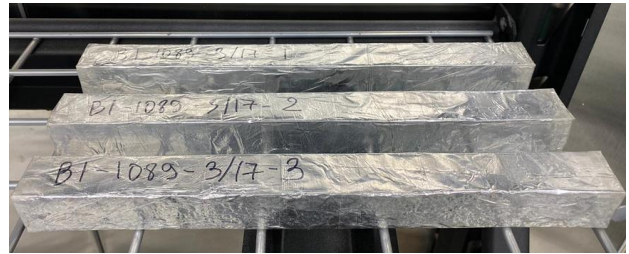
For the first set of the samples, ASTM C157 (Standard Test Method for Length Change of Hardened Hydraulic-Cement Mortar and Concrete) was followed to determine the change of length of cement mortar caused by drying shrinkage. Three specimens were prepared for each mix design using prism molds (1 in × 1 in × 11 1/4 in) and then cured in lime-saturated water for 28 days. Shrinkage bars then should be stored in the environmental chamber (with a controlled temperature level of $73.5 \pm 5.5^{\circ}\text{F}$ ($23.0 \pm 3.0^{\circ}\text{C}$) and the Relative Humidity of $50 \pm 4\%$) and be measured after 4, 7, 14, and 28 days, and after 8, 16, 32, and 64 weeks.

For the second condition, the prism samples of the same dimensions and amount were securely wrapped in a foil and tape to minimize the moisture loss and were immediately placed in the environmental chamber where the length change

measurements were taken at 4, 7, 14, and 28 days, and after 8, 16, 32, and 64 weeks counted from the mixing date.



a) LVDT sensor to measure the length



b) Samples sealed with foil and tape

Figure 3.22. Length change measurement setup

3.5.4. Resistance to chloride ion penetration (Electrical resistivity)

The resistance of hardened concrete to chloride ion penetration was measured by means of AASHTO TP 95-14 (Standard Method of Test for Surface Resistivity Indication of Concrete's Ability to Resist Chloride Ion Penetration), when the measurement of electrical surface and bulk resistivity of fully saturate cylindrical specimens (4 in $\times$ 8 in) was performed using Proceq Resipod equipment at ages of 1,3,7,14 and 28 days.



a) Surface resistivity



b) Bulk resistivity

Figure 3.23. Proceq Resipod apparatus for concrete electrical resistivity testing

3.6. CO₂ treatment

The following section will describe the CO₂ treatment procedure of raw materials (biochar and LWFA) and fresh mortar specimens, their storing/curing conditions, and the approach to estimating the amount of the CO₂ that was absorbed/released.

3.6.1. Procedure of CO₂ treatment of biochar

A sample of biochar (or LWFA) that was initially dried in the oven at $110\pm5^{\circ}\text{C}$ (presumably to empty all the pores from any water molecules so the CO₂ will be able to occupy as many pores as it can) and then cooled down to a room temperature $73.5\pm5.5^{\circ}\text{F}$ ($23.0\pm3.0^{\circ}\text{C}$) was placed in a proposed setup (Figure 3.24):

- i. The material was placed on top of No.100 (150 microns) sieves to ensure free access of the gas from both top and bottom.
- ii. A hollow (2 in x 1.5 in) cylinder was placed in the center of the sieve to provide a free gas flow (pressure balance) in case if sieve's openings are blocked by material particles
- iii. The pan placed at the bottom is used to collect those biochar particles that will pass No.100 sieves
- iv. The top sieve is used to minimize the loss of particles from the top of the setup

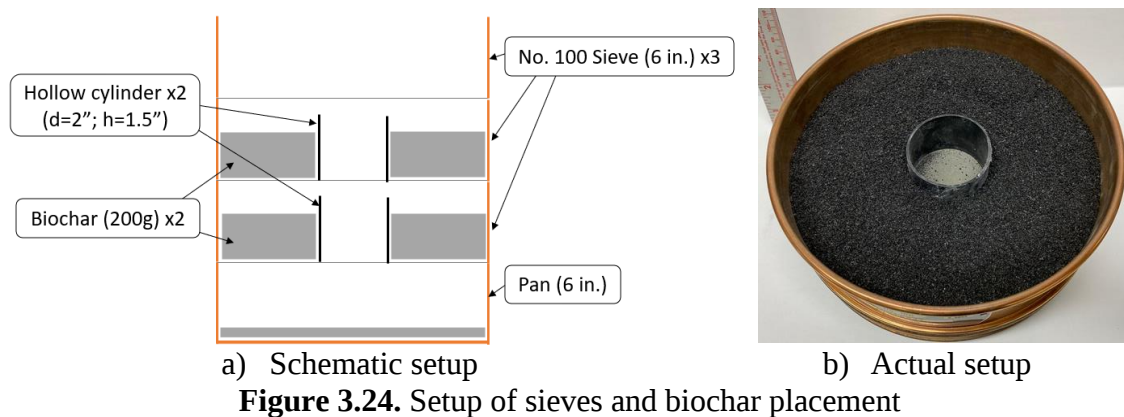


Figure 3.24. Setup of sieves and biochar placement

The sample was then placed in a 10-L treatment steel tank (Figure 3.25).

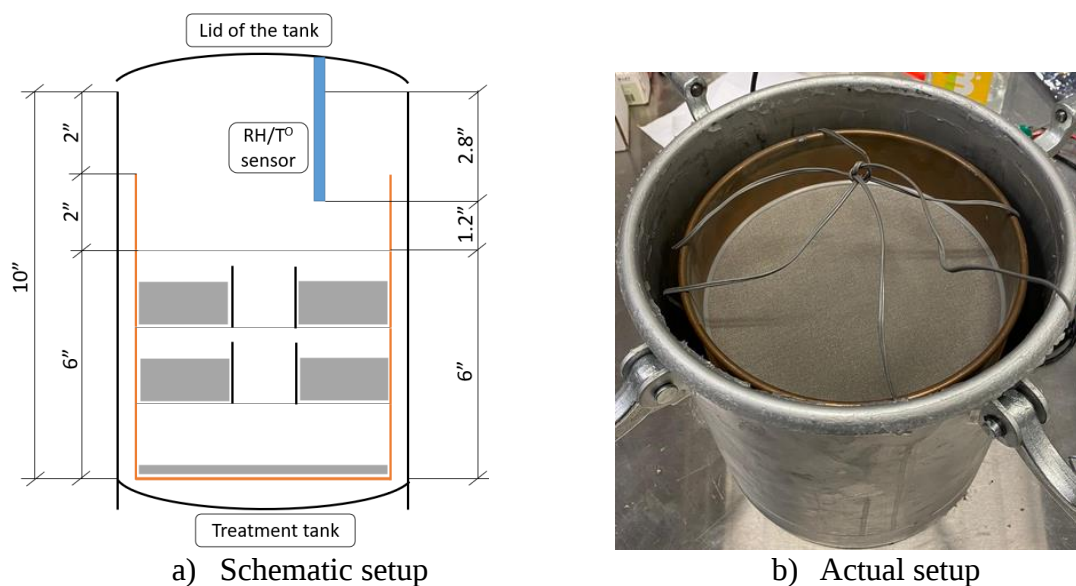


Figure 3.25. Placing biochar in the treatment tank



Figure 3.26. The complete setup includes: compressed CO₂ source; steel tank; 5-V power supply; data logger

The air was then evacuated, and a pure CO₂ gas was applied at different pressure levels, while temperature, pressure, and relative humidity levels were measured and recorded. The treated material was then weighted and put in a sealed plastic bag immediately after finishing the treatment process until the moment it was introduced to the mix (Figure 3.27). As can be seen from the figure, a portion of the CO₂ gas started to release from the material as the bag apparently swelled after one day of storing under normal pressure. That is why it was decided to introduce biochar into the mix immediately after finishing the treatment process.



a) Immediately after the treatment



b) One day after the treatment

Figure 3.27. Treated biochar in a sealed plastic bag

3.6.2. Procedure of CO₂ treatment of concrete

A treatment procedure of fresh concrete specimens does not much differ from the proposed treatment of biochar (section 3.6.1). Ten 2×2×2-in mortar samples were subjected to a CO₂ treatment immediately after demolding (24 hours after mixing). In addition, silica gel was used to control the relative humidity level inside of the treatment tank so that excessive moisture would not demote the diffusion of CO₂ molecules.

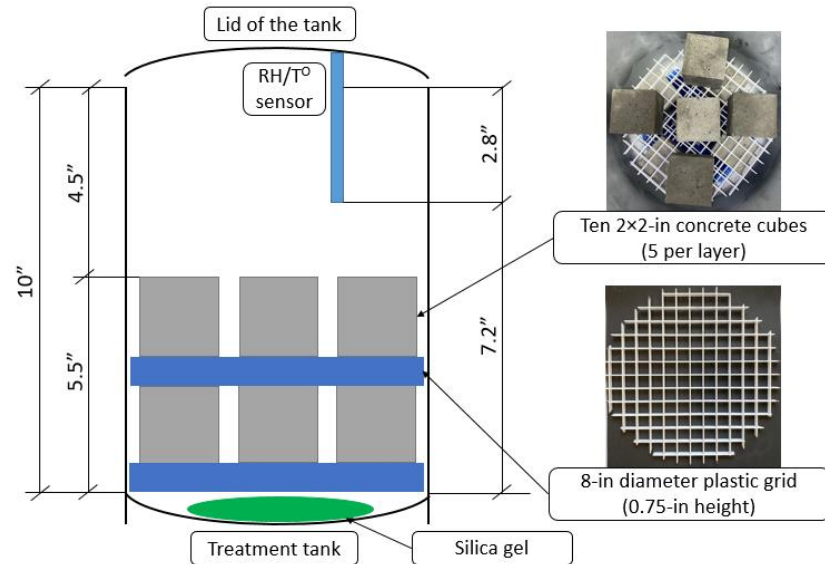


Figure 3.28. Setup for the carbonation of fresh concrete specimens

The rest of the procedure was similar to biochar treatment, except that the specimens were weighed and subjected to vacuum sealing immediately after the treatment was completed. In addition, one mortar specimen was broken in half, so that the internal cross-section might be exposed to the application of phenolphthalein – a colorless pH indicator, which changes its color to pink when in contact with a basic (alkaline) environment.

3.6.3. Estimation of the amount of the CO₂ absorbed/released

3.6.3.a. Mass difference method

A mass of the sample was measured before and after the treatment, so the mass difference presumably indicates the amount of the CO₂ absorbed by the material. Note that for the treatment of biochar (not concrete specimen) moisture gain can be ignored as the sample was initially oven-dried, and the pure CO₂ gas is supposed to be free of moisture.

$$\text{CO}_2 \text{ absorbed} = W_{\text{after treatment}} - W_{\text{before treatment}} \quad (\text{eq. 3.3})$$

Similarly, the weight of the treated material was measured right before introducing it in a concrete mix to estimate the amount of CO₂ loss.

$$\text{CO}_2 \text{ released} = W_{\text{after treatment}} - W_{\text{before mixing}} \quad (\text{eq. 3.4})$$

3.6.3.b. Real Gas Law concept – van der Waals model

As the temperature and pressure level values were measured throughout the whole process of the treatment, they were used to apply the real gas law concept (Van der Waals model) to estimate the amount of the CO₂ molecules absorbed based on the continuous pressure drop.

$$(P + an^2/V^2) \times (V - nb) = nRT \quad (\text{eq. 3.5})$$

P – pressure value at a given time point

V – volume of the treatment tank (excl. the vol. of the material and inner container)

a – correction factor for attractive forces between CO₂ gas molecules (0.364 L²bar/mol²)

b – correction factor for the volume of the CO₂ molecules (0.04267 L/mol)

n – amount of substance of the gas (mol)

R – gas constant (8.31 J K⁻¹mol⁻¹)

T – temperature of the gas (K)

Thus, applying and solving the Van der Waals equation (3.5) for the amount of substance of the gas (n) and monitoring its change throughout the whole treatment process, the amount of the CO₂ absorbed can be estimated as:

$$\text{CO}_2 \text{ absorbed} = (n_{\text{initial}} - n_{\text{at time t}}) \times \text{Molar mass} \quad (\text{eq. 3.6})$$

However, several assumptions were made to apply this concept, which might be critical for the calculations. Firstly, it was supposed that the gas inside the treatment chamber consists of only the pure CO₂ gas, whereas in reality, it might happen that not all the air was evacuated before the treatment. Secondly, the pressure drop was measured

once it reached the peak value, thereby ignoring the fact that the material started to absorb the CO₂ immediately after beginning the CO₂ injection in a tank.

3.6.3.c. Rate of CO₂ release by measuring gas concentration

The amount and rate of the CO₂ release can be estimated by monitoring the release of initially entrapped CO₂, which is based on measuring a change in CO₂ concentration in a sealed 4-L container. A 1.5-g sample of treated biochar (immediately after the treatment process) was placed in a sealed container with a sensor, which was used to continuously measure CO₂ concentration inside of the container. Measurements were taken every 5 minutes during the first 30 minutes of the test, followed by measurements taken at 1, 2, 3, 6, 12, 24, 48-hour time marks. This test was performed to estimate how much of the initially absorbed CO₂ might be lost before introducing treated biochar into a concrete mix, as well as what portion of the absorbed CO₂ might be potentially released for the internal carbonation inside of the biochar.

A similar approach was used to monitor CO₂ release from the treated concrete sample, which was placed in the same setup. In this case, a peak CO₂ concentration value was used to calculate the amount of the released CO₂, which was then subtracted from the estimated absorbed CO₂ (section 3.6.3.b) to estimate an effective amount of the absorbed CO₂ that was actually used for the carbonation mechanism.

Nevertheless, both methods may imply a major drawback of not taking into account the potential CO₂ release in between finishing the treatment process and starting of the test (the gas might be released when the pressure in the chamber is started being reduced).



a) Treated biochar sample

b) Treated mortar specimen

Figure 3.29. Setup to measure CO₂ desorption from (a) treated biochar sample and (b) treated concrete specimen

CHAPTER 4. EXPERIMENTAL PROGRAM AND RESULTS

This chapter is purposed to present the details of the experimental program and the results of this study, which were divided into several subsections based on the objective of each biochar application.

The first step was to identify the influence of biochar applied as an additive in the mortar (the common approach by previous researchers, however, in a much wider range of 1-20%). Once the effects of biochar content and fineness were identified, the next step was to actually replace the cement with biochar in a high range, where the reduction of cement will be significant (more than 5-10%). The next step of the experimental program was the attempt to apply a low content of biochar (1-2.5%) in mortar mixes with a considerably lower cement content (reduction up to 20%). Finally, a few other implications of biochar for internal curing and carbonation of the mortar were attempted.

In addition, a set of concrete mixtures was prepared to study the effect of biochar on concrete fresh and mechanical properties, as well as to study the possibility of the aggregate-cement paste bond improvement as a result of the biochar application.

4.1. Biochar as an additive in mortar

The focus of this part of the project was to identify the influence of biochar directly introduced to the mix at different dosage and fineness levels on the fresh and mechanical properties of the hydraulic cement mortar when additional water demand of the biochar particles was not taken into account in the same manner as it was commonly performed by other researchers.

4.1.1. Mix design approach and proportions

Mix design approach I (oven-dry biochar as an additive): it was commonly acceptable to introduce a certain amount of the biochar in the mix measured by % weight of the cement, but without the actual replacement of the cement and any mix water adjustment due to additional water demand of the biochar (Restuccia and Ferro, 2016; Cosentino et al., 2018; Gupta et al., 2017; Gupta et al., 2018a; Gupta et al., 2018b). However, this approach could still imply the reduction of the actual amount of all other ingredients (per cubic yard of concrete), including the cement amount, as the volume occupied by the additional material (biochar) was not initially accounted for in mix design and the final amount of the concrete mortar produced will be greater than for the designed control batch. Additionally, the mix may end up with a reduced effective water-to-cement ratio due to the extra water demand implied by the high water absorption properties of biochar.

This approach was used in combination with the premixing of dry biochar and cement, as was described in a previous section.

At this stage, a corn stover biochar (B2) was chosen (due to time and material availability) to be the base material to be used at a wide range of the dosage (1-20% by weight of cement) and three fineness degrees (original, ground and highly-ground) to study the effect of the biochar content and fineness, as well as to identify a potential recommended optimum to be applied for the other remaining biochar samples.

The recommended optimum dosage was also confirmed by applying the same testing range for a single fineness degree of distillers grain biochar (B1), given a

comparison of the selected fineness degree with the original material for one of the dosages (B1-C10% vs. B1G1-C10%).

Table 4.1. Biochar as an additive in mortar - Mix proportions

Mix ID	Cement (pcy)	Water (pcy)	Sand (pcy)	Biochar (pcy)	SP (fl.oz/cwt)
Control	904 947*	389 408*	2487 2606*	-	-
B2 – Corn Stover Biochar					
B2-C1%	904 960*	389 413*	2487 2640*	9 10*	-
B2-C2.5%	904 941*	389 405*	2487 2588*	23 24*	2.0
B2-C5%	904 925*	389 398*	2487 2546*	45 46*	
B2-C10%	904 913*	389 393*	2487 2512*	90 91*	10.0
B2-C15%	904 912*	389 393*	2487 2510*	136 137*	18.0
B2-C20%	904 894*	389 385*	2487 2458*	181 179*	25.0
B2G1-C1%	904 959*	389 413*	2487 2640*	9 10*	-
B2G1-C2.5%	904 948*	389 408*	2487 2608*	23 24*	-
B2G1-C5%	904 932*	389 401*	2487 2564*	45 46*	2.0
B2G1-C10%	904 913*	389 393*	2487 2511*	90 91*	8.0
B2G1-C15%	904 921*	389 396*	2487 2533*	136 139*	16.0
B2G1-C20%	904 902*	389 388*	2487 2482*	181 181*	28.0
B2G2-C1%	904 959*	389 413*	2487 2639*	9 10*	-
B2G2-C2.5%	904 942*	389 405*	2487 2591*	23 24*	2.0
B2G2-C5%	904 937*	389 403*	2487 2578*	45 47*	2.0
B2G2-C10%	904 917*	389 395*	2487 2522*	90 91*	8.0
B2G2-C15%	904 911*	389 392*	2487 2506*	136 137*	19.0

B2G2-C20%	904 896*	389 386*	2487 2466*	181 179*	22.0
B1 – Distillers Grain Biochar					
B1G1-C1%	904 954*	389 410*	2487 2623*	9 9*	-
B1G1-C2.5%	904 942*	389 405*	2487 2591*	23 24*	-
B1G1-C5%	904 926*	389 399*	2487 2548*	45 46*	-
B1G1-C7.5%	904 918*	389 395*	2487 2527*	68 69*	2.0
B1G1-C10%	904 916*	389 394*	2487 2521*	90 91*	2.0
B1G1-C15%	904 878*	389 378*	2487 2416*	136 132*	7.0
B1G1-C20%	904 858*	389 369*	2487 2361*	181 172*	15.0
B1-C10%	904	389	2487	90	5.0

* True mix design proportions based on the fresh unit weight value (necessary for the mixes where the specific gravity of biochar was not specified)

4.1.2. Influence on fresh mortar properties

The results of fresh concrete properties testing are summarized in the following table:

Table 4.2. Biochar as an additive in mortar - Fresh mortar properties

Mix ID	Flow (%)	SP (fl.oz/ cwt)	Unit Weight (pcf)	Setting time (hrs)		Heat of Hydration (J/g of cement)	
				Initial	Final	24-hr	72-hr
Control	113	-	146	4.8	7.8	200	275
B2 – Corn Stover Biochar							
B2-C1%	110	-	149	4.5	7.5	208	283
B2-C2.5%	87 (107*)	2.0	147	5.7	8.3	209	292
B2-C5%	89 (109*)	5.0	145	6.6	8.0	206	314
B2-C10%	52 (105*)	10.0	145	7.1	11.4	185	301
B2-C15%	117*	18.0	147	7.0	10.5	228	294
B2-C20%	119*	25.0	146	9.9	12.8	215	281
B2G1-C1%	113	-	149	4.7	7.5	207	275
B2G1-C2.5%	113	-	148	5.6	8.2	205	283
B2G1-C5%	100 (113*)	2.0	146	5.8	8.1	204	279
B2G1-C10%	115*	8.0	145	5.8	9.2	224	285

B2G1-C15%	120*	16.0	148	5.8	9.2	229	292
B2G1-C20%	134*	28.0	147	8.9	12.3	221	293
B2G2-C1%	109	-	149	5.1	7.6	203	276
B2G2-C2.5%	100 (111*)	2.0	147	5.1	7.6	210	289
B2G2-C5%	98 (111*)	2.0	147	5.4	7.9	214	294
B2G2-C10%	113*	8.0	146	5.6	9.5	226	296
B2G2-C15%	124*	19.0	147	7.6	11.2	222	290
B2G2-C20%	112*	22.0	146	8.2	12.2	217	284
B1 – Distillers Grain Biochar							
B1G1-C1.0%	114	-	148	3.6	6.4	219	309
B1G1-C2.5%	109	-	147	4.6	7.6	203	283
B1G1-C5%	106	-	139	4.8	7.7	210	294
B1G1-C7.5%	96 (108*)	2.0	145	5.1	7.8	213	297
B1G1-C10%	95 (106*)	2.0	145	5.0	7.9	205	281
B1G1-C15%	115*	7.0	141	5.1	9.5	229	329
B1G1-C20%	109*	15.0	140	11.5	14.4	167	267
B1-C10%	51 (102*)	5.0	135	5.3	7.8	198	270

*Flow measured after the application of superplasticizer

Influence on workability

As can be seen from the table, a common trend of the workability reduction and a consequent higher demand in a superplasticizer dosage (with the increase in the biochar content) was observed for all three fineness levels of B2 biochar mixes, apparently, due to increasing extra water demand accounted for an increasing amount of biochar particles. The same was observed for B1-mixes, although the workability drop was lower than for B2, which possibly indicates lower water retention properties of corn stover biochar.

However, the effect of biochar fineness degree on the workability was not that apparent. At first, the comparison between original and ground biochar (for both B1 and B2) shows that grinding helps to reduce the negative impact of biochar addition on the flowability of mortar. This may potentially be explained by the fact that despite the increase of the number of biochar particles (and subsequent increase in net surface area),

the cumulative water absorption capacity of the internal pores is higher for the original coarse biochar sample, implying the fact that the micropore structure of biochar particles is being destroyed due to grinding, which was also experimentally confirmed by Choi et al. (2012). However, it seems that for the highly-ground biochar (B2G2), an increased surface area of the biochar particles was a more prevailing factor, and that resulted in lower workability than for B2G1.

Influence on hydration

The addition of both biochar samples resulted in a higher peak of hydration power, and, as a result, in a higher value of generated heat of hydration (per gram of cement) for both 24 and 72-hour time periods with a general trend of increasing the value with the increased fineness or higher biochar content, which may imply the reactivity of biochar, as well as the fact that the hydration is potentially enhanced due to the presence of biochar particles that act as additional hydration nucleation sites.

Regarding the setting, it might be more accurate to compare the estimated setting time values for the mixes different in biochar fineness degree, rather than between the mixes with different biochar contents, as the latter ones require a higher amount of superplasticizer admixture, which largely affects setting (with a general rule of delayed setting when SP is applied). Thus, it can be seen that an increase in biochar fineness degree resulted in a more sudden setting, possibly due to a higher probability of biochar particles to act as additional nucleation points when the number of particles themselves is higher (finer biochar implies a larger amount of individual particles for the same mass of the material).

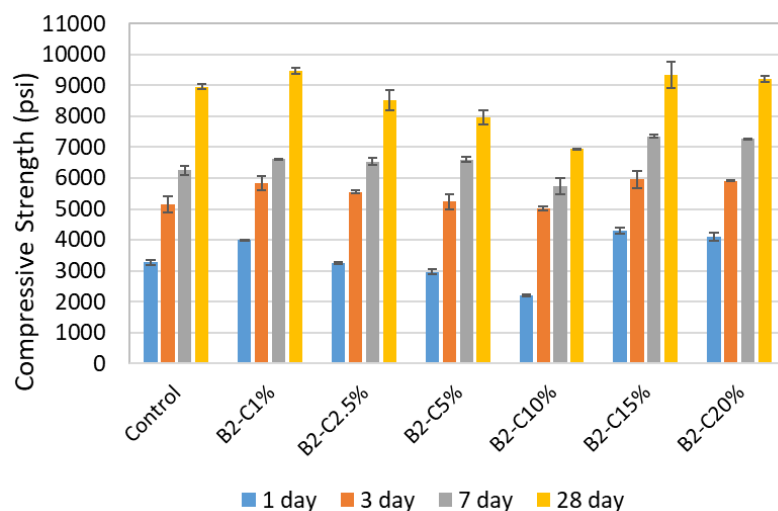
4.1.3. Influence on mortar strength

Effect of biochar content

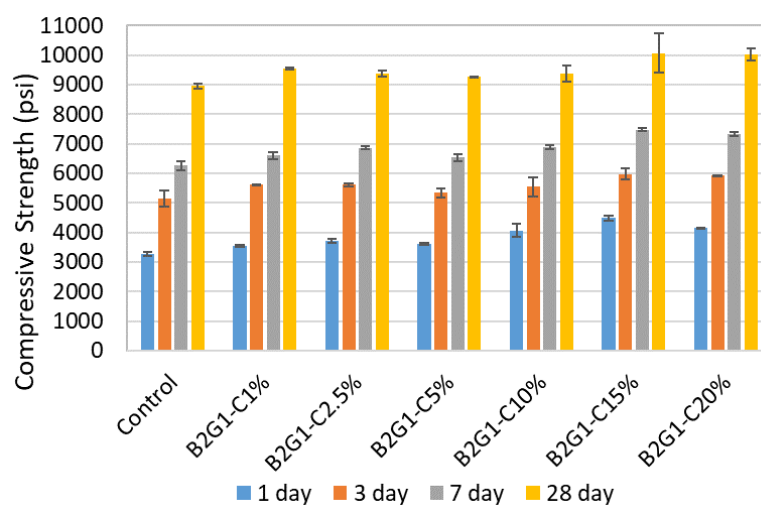
As can be seen from Figure 4.1, where the effect on the compressive strength at different biochar dosages (separated by biochar type and fineness degree) was illustrated, the addition of biochar resulted in a noticeable early age strength improvement, which then became less apparent at a later age. This might be explained by the enhanced hydration as biochar particles potentially act as additional nucleation sites during the early cement hydration (confirmed by the heat of hydration results from the previous subsection), which is later outbalanced by the weak and brittle nature of the particles, as well as the reduced unit content of cement.

Interestingly, the addition of biochar generally resulted in an increase of the strength in a pattern general for all four sets of mixes: having two peaks of strength increase at low content (around 1.0-2.5%) and considerably higher dosage (around 15%). This presumably might be explained by the fact that for a low biochar content (up to 2.5%), when biochar's additional water demand does not significantly influence effective w/c ratio (as confirmed by workability testing), potential better particles packing and nucleation effects are more prevailing factors towards the strength increase, which then are being compromised by the weak nature of particles and lower cement amount per unit volume of mortar (around 5%), whereas a further increase in strength (up to 15%) can be attributed to a significantly lower effective water-to-cement ratio (when additional water demand of biochar starting to have a significant impact), followed by the same phenomenon of weaker particles and cement reduction (past 15%). Moreover, the pattern

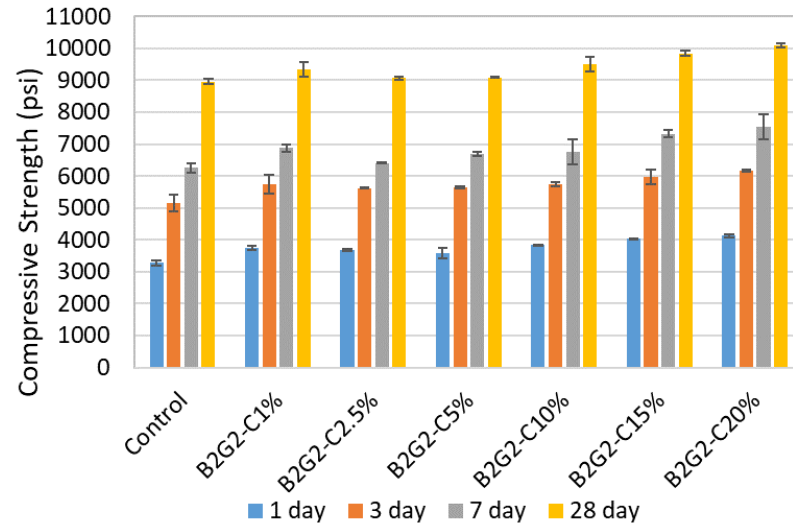
was common for all of the presented biochar mixes regardless of fineness (B2, B2G1 and B2G2) and biochar type (B1 and B2).



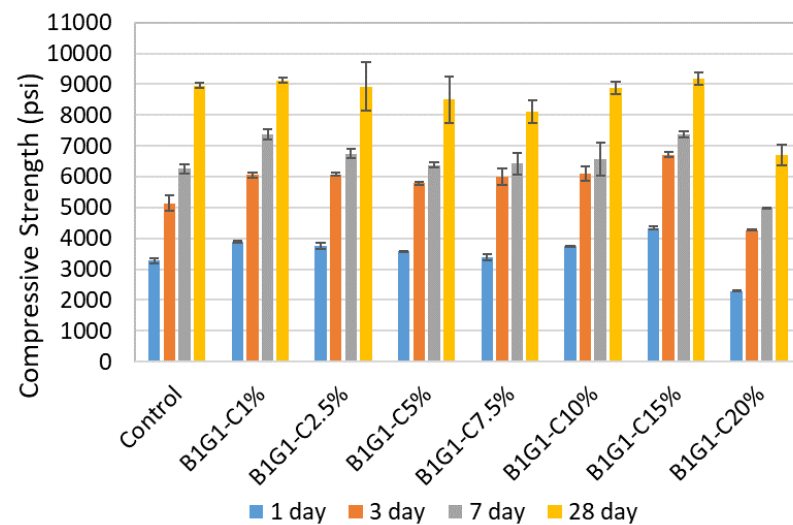
a) Different content of B2



b) Different content of B2G1



c) Different content of B2G2

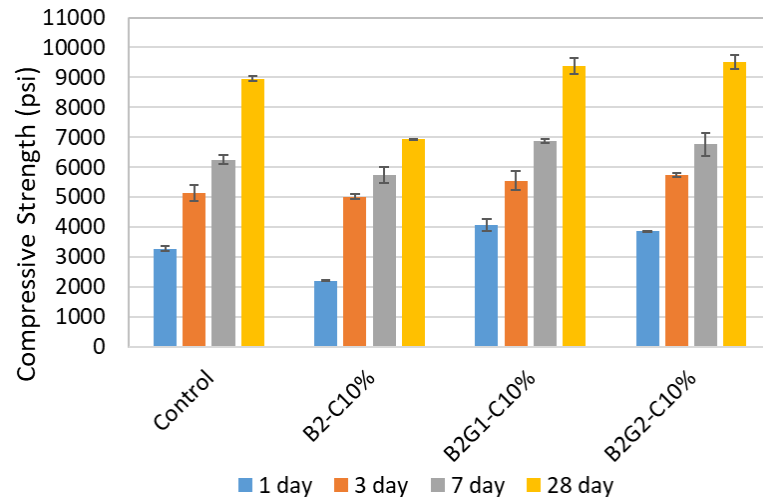


d) Different content of B1G1

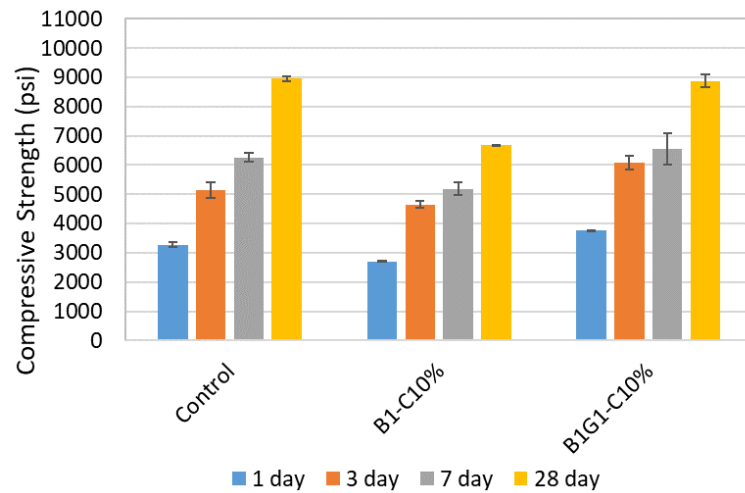
Figure 4.1. Biochar as an additive in mortar - Effect of biochar content on compressive strength

Effect of biochar fineness

As was expected, grinding the biochar resulted in an improved positive effect on mortar strength properties, as a finer biochar sample implies a presence of a greater amount of additional nucleation points and potential better packing (smaller particles may occupy potential space voids in a mortar matrix).



a) Different fineness of B2



b) Different fineness of B1

Figure 4.2. Biochar as an additive in mortar - Effect of biochar fineness on compressive strength

Overall, based on the presented results, two biochar dosage levels were selected to be optimal:

- 1-2.5% with a fair increase in compressive strength without any significant compromise in workability (attributed to nucleation and filler effects)

- Around 15% with a significant strength improvement which also required a high dosage of superplasticizer to maintain a desirable flowability of the mix (attributed to the reduced effective water-to-cement ratio and nucleation effects to be factors more prevailing than cement dilution and weak nature of biochar particles)

4.2. Biochar as a partial cement replacement in mortar

The main goal of this part of the experimental program was to study of the effect of the direct replacement of cement with biochar (by weight). Since the reduction of cement at low dosage would not have significant benefits from environmental and economic points of view, the cement content of mortar mixes was significantly reduced (10-20% reduction) and directly substituted (by weight) with biochar of different sources: corn stover (B2), waste wood (B3) and red cedar (B4).

4.2.1. Mix design approach and proportions

Mix design approach 2 (oven-dry biochar as a cement replacement by weight): this method was used for the preparation of the mortar mixes with the reduced cement content, where a certain amount of cement was replaced by weight percentage with biochar, which was considered as supplementary cementitious material so that the amount of mixing water was adjusted to keep a constant: A) 0.43 water-to-binder ratio and B) 0.43 water-to-cement ratio.

This approach was used in a combination with the premixing of dry biochar and cement as was described in a previous subsection.

Table 4.3. Biochar as cement replacement - Mix proportions

Mix ID	Cement (pcy)	Water (pcy)	Sand (pcy)	Biochar (pcy)	SP (fl.oz/cwt)	w/c ratio	w/b ratio ²
Control	904 947 ¹	389 408 ¹	2487 2606 ¹	-	-	0.430	0.430
B2 – Corn Stover Biochar							
B2G1-R5%_A	859 899 ¹	389 407 ¹	2487 2602 ¹	45 47 ¹	-	0.453	0.430
B2G1-R10%_A	814 837 ¹	389 400 ¹	2487 2557 ¹	90 93 ¹	4.0	0.478 0.480 ³	0.430 0.432 ³
B2G1-R15%_A	769 788 ¹	389 398 ¹	2487 2547 ¹	136 139 ¹	7.0	0.506 0.510 ³	0.430 0.433 ³
B2G1-R10%_B	814 856 ¹	350 368 ¹	2487 2614 ¹	90 95 ¹	8.3	0.430 0.434 ³	0.387 0.391 ³
B2G1-R15%_B	769 825 ¹	331 355 ¹	2487 2668 ¹	136 146 ¹	18.0	0.430 0.442 ³	0.366 0.375 ³
B2G1-R20%_B	723 817 ¹	311 338 ¹	2487 2699 ¹	181 196 ¹	33.4	0.430 0.450 ³	0.344 0.360 ³
B3 – Waste Wood Biochar							
B3G2-R10%_B	814 817 ¹	350 365 ¹	2487 2595 ¹	90 94 ¹	13.6	0.430 0.437 ³	0.387 0.394 ³
B3G2-R15%_B	769 817 ¹	331 352 ¹	2487 2641 ¹	136 144 ¹	41.7	0.430 0.454 ³	0.366 0.386 ³
B3G2-R20%_B	723 754 ¹	311 324 ¹	2487 2593 ¹	181 189 ¹	73.8	0.430 0.474 ³	0.344 0.379 ³
B3G1-R15%_B	769 809 ¹	331 348 ¹	2487 2616 ¹	136 143 ¹	52.2	0.430 0.460 ³	0.366 0.391 ³
B4 – Red Cedar Biochar							
B4-R10%_B	814 846 ¹	350 364 ¹	2487 2586 ¹	90 94 ¹	11.8	0.430 0.436 ³	0.387 0.393 ³
B4-R15%_B	769 803 ¹	331 346 ¹	2487 2597 ¹	136 142 ¹	43.1	0.430 0.455 ³	0.366 0.386 ³
B4G1-R10%_B	814 868 ¹	350 373 ¹	2487 2652 ¹	90 96 ¹	12.5	0.430 0.436 ³	0.387 0.393 ³

¹True mix design proportions based on the fresh unit weight value (necessary for the mixes where the specific gravity of biochar was not specified)

²when biochar is considered as a part of a binder

³w/c or w/b when the amount of additional water due to SP application is accounted

4.2.2. Influence on fresh mortar properties

The table below summarizes the results of the fresh mortar properties test of the set of mixes with biochar as a cement replacement:

Table 4.4. Biochar as cement replacement - Fresh mortar properties

Mix ID	Flow (%)	SP (fl.oz/cwt)	Unit Weight (pcf)	Setting time (hrs)		Heat of Hydration (J/g of cement)	
				Initial	Final	24-hr	72-hr
Control	113	-	146	4.8	7.8	200	275
B2 – Corn Stover Biochar							
B2G1-R5%_A	114	-	146	6.1	8.4	207	287
B2G1-R10%_A	87 (116*)	4	144	6.2	9.1	216	299
B2G1-R15%_A	106*	7	144	6.4	10.6	225	304
B2G1-R10%_B	111*	8.3	146	5.1	9.1	240	325
B2G1-R15%_B	114*	18.0	148	7.0	10.7	232	308
B2G1-R20%_B	119*	33.4	150	11.0	13.3	235	327
B3 – Waste Wood Biochar							
B3G2-R10%_B	125*	13.6	145	4.4	9.1	247	343
B3G2-R15%_B	128*	41.7	147	7.4	11.4	231	331
B3G2-R20%_B	104*	73.8	145	13.0	15.5	211	324
B3G1-R15%_B	105*	52.2	146	9.1	13.5	224	336
B4 – Red Cedar Biochar							
B4-RC10%_B	104*	11.8	144	4.3	8.9	246	336
B4-RC15%_B	104*	43.1	145	8.4	12.4	229	336
B4G1-RC10%_B	120*	12.5	148	4.8	9.3	237	325

*Flow measured after the application of superplasticizer

Overall, the proposed mix proportions of the batches with the reduced cement content implied by replacing it with biochar resulted in batches with fair fresh mortar properties, characterized by a generally delayed setting (depending on the biochar type), enhanced hydration (as can be seen from the generated heat of hydration data) and decreased workability.

Influence on workability

As can be seen from table 4.4, the workability of the mortar mixes was not as significantly affected for the mixes where the biochar water absorption properties were taken into account in a manner when biochar was considered to be a part of a binder and

the water-to-binder ratio was attempted to be kept constant (approach B), resulting in the demand of the superplasticizer below average recommended dosage. Whereas for the set of mixes where the additional water demand of biochar particles was not considered (approach A), the increase in biochar replacement rate dramatically raised the demand in superplasticizer, reaching extremely high dosage requirements for mixes with 15-20% of cement replacement.

Influence on setting and hydration

Similar to the mixes from the previous part of the experimental program, it seems that the generally delayed mortar setting was a result of a high dosage of the superplasticizer added to the mixes with higher biochar content.

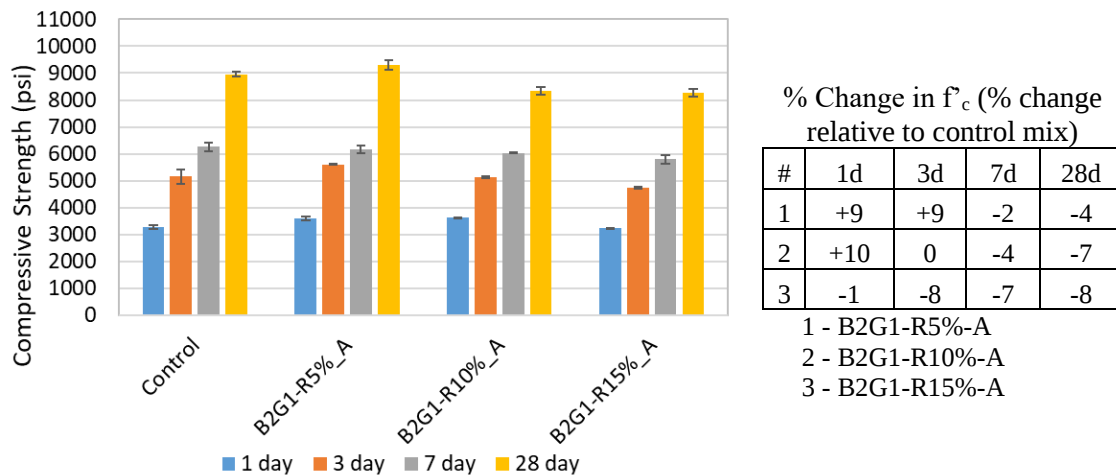
In addition, biochar addition resulted in enhanced hydration (based on the generated heat of hydration measurement), although it may not necessarily imply the overall improvement of the whole mortar hydration as those measurements are performed per gram of cement, and the actual initial less amount of cement in the mix may result in fewer hydration products production (dilution effect). However, an apparent sign of the nucleation effect can still be observed (enhanced hydration per g of cement).

4.2.3. Influence on mortar strength

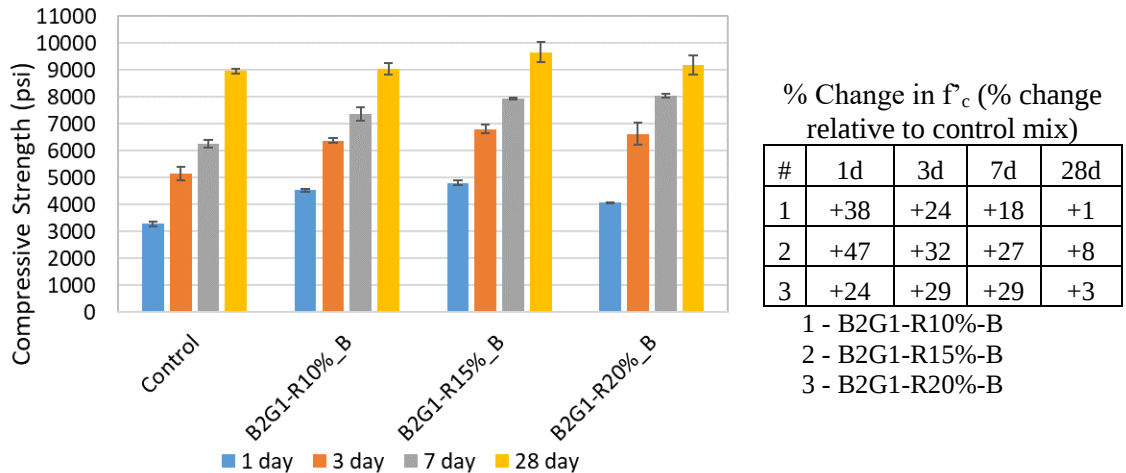
Despite a slight early strength improvement accounted for a possible nucleation effect, the replacement of the cement with biochar (for approach A) resulted in the decrease of the compressive strength of the mortar for 7- and 28-days values (Figure 4.3.a). The negative impact increased with an increase in the replacement rate, implying

the bigger influence of a lower cement paste amount and higher content of weaker biochar particles.

The trend was different for the second mix design approach (B), when additional water demand of biochar particles was not taken into account (Figure 4.3.b). In this case, the replacement of cement with biochar still ended up with an improvement in mortar's early strength but in a considerably higher manner, implying the effect of the reduced effective water to cement ratio due to high water absorption properties of biochar (in addition to the nucleation effect), which was partially compromised with lower cement paste content at a later stage. In addition, the results suggested a presence of an optimum replacement rate of 15% (for B2G1). As for this dosage, the positive impact from the reduced effective w/c ratio and addition nucleation outbalanced the reduced cement content the most.

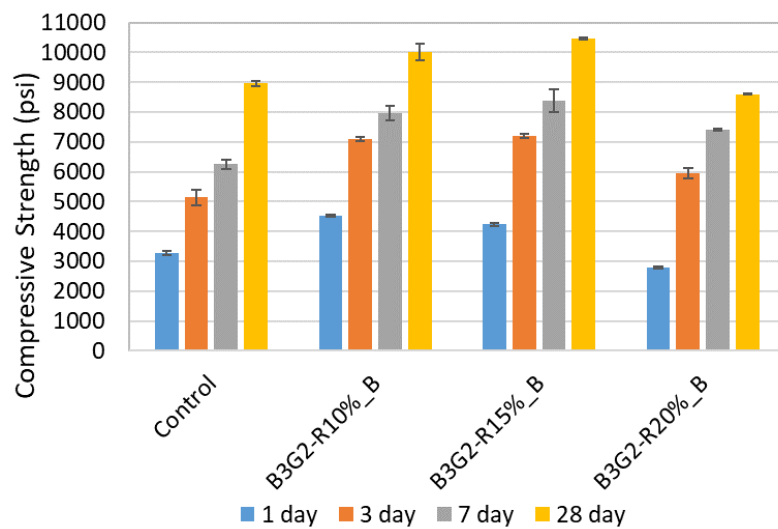


a) B2G1 – as cement replacement (mix design approach A)

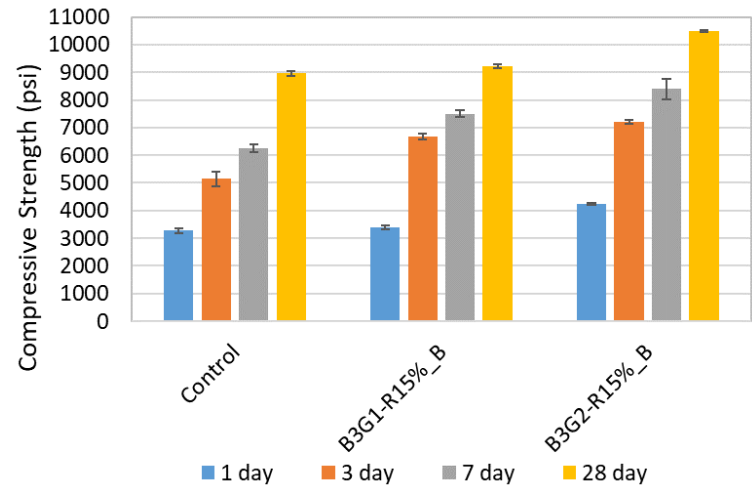


b) B2G1 – as cement replacement (mix design approach B)
Figure 4.3. Biochar as cement replacement - Effect of the cement replacement amount/mixing approach on compressive strength – B2G1

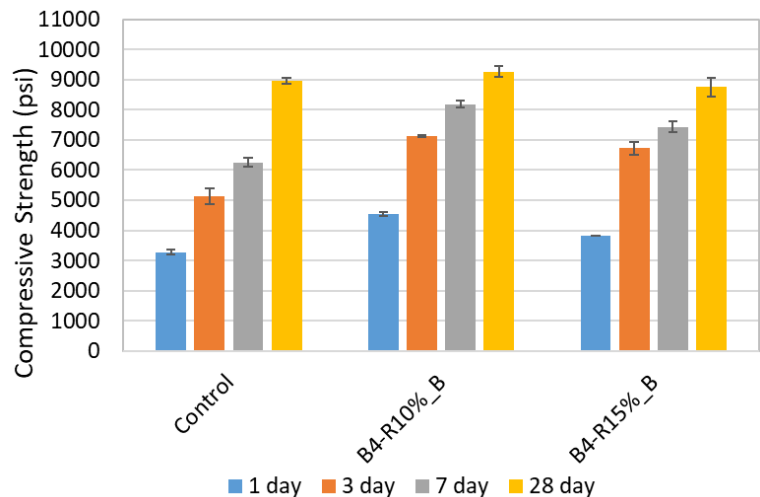
The same trend but with slightly different optimum dosage values (in a range of 10-15%) was achieved for the mixes where cement was replaced with waste wood (B3) and red cedar (B4) biochar samples (Figure 4.4.a and 4.4.c). Moreover, similar to the study described in the previous subsection (biochar as an additive in mortar), finer biochar samples ended up with a better mechanical performance of the mix they were added in (Figure 4.4.b and 4.4.d).



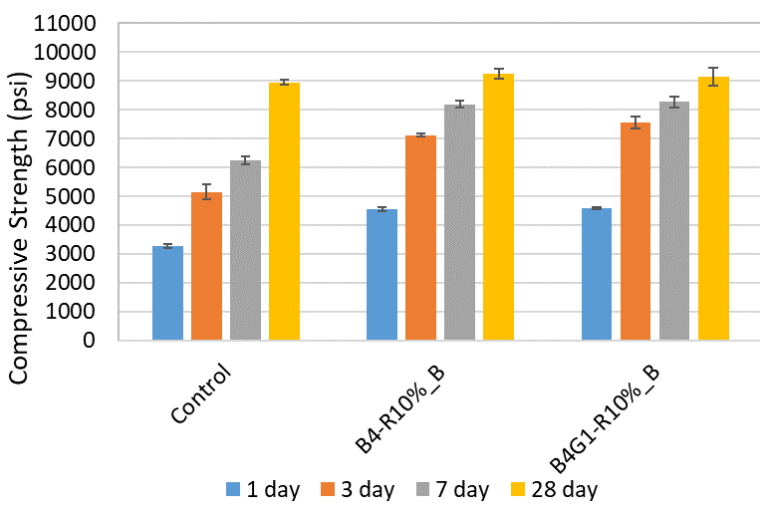
a) B3G2 – effect of the replacement rate



b) B3 – effect of the fineness degree



c) B4 – effect of the replacement rate



d) B4 – effect of the fineness degree

Figure 4.4. Biochar as cement replacement – Effect of the replacement amount/ biochar fineness on compressive strength – B3 and B4

4.3. Biochar as an additive in mortar with reduced cement content

Even though the previous part of the study revealed a possibility of a significant improvement of the compressive strength of concrete, when cement is replaced with biochar at high dosages (also required an extremely high dosage of superplasticizer to maintain a comparable workability level), this strength increase might not be necessarily needed if the minimum strength requirements of the concrete are met. The main objective of this part of the study was to develop a set of mortar mixes with the reduced cement content, the potentially impaired mechanical properties of which are attempted to be compensated with the use of biochar as an additive at a low dosage.

4.2.1. Mix design approach and proportions

The mix design approach and the mixing procedure of this part of this study are similar to the one described in section 4.3 (oven-dry biochar as an additive). Thus, a low content of biochar that was considered to be an optimum effective dosage in the previous study (1-2.5% by weight of cement) was introduced into the mortar with a 10,15, and 20% reduction in cement content.

Table 4.5. Biochar as an additive in reduced cement mortar - Mix proportions

Mix ID	Cement (pcy)	Water (pcy)	Sand (pcy)	Biochar (pcy)	SP (fl.oz/cwt)
Control	904 947*	389 408*	2487 2606*	-	-
10% cement reduction					
Control-R10	814 840 ¹	350 361 ¹	2685 2772 ¹	-	2.2
B3G2_R10_B1	814 844 ¹	350 363 ¹	2685 2784 ¹	23 24 ¹	2.1
B3G2_R10_B2.5	814 841 ¹	350 362 ¹	2685 2774 ¹	23 24 ¹	3.0
15% cement reduction					

Control-R15	769 789 ¹	331 340 ¹	2784 2858 ¹	-	3.8
B3G2_R15_B1	769 781 ¹	331 336 ¹	2784 2829 ¹	9 9 ¹	3.8
B3G2_R15_B2.5	769 782 ¹	331 337 ¹	2784 2833 ¹	23 23 ¹	4.3
20% cement reduction					
Control-R20	723 741 ¹	311 319 ¹	2861 2931 ¹	-	4.7
B3G2_R20_B1	723 730 ¹	311 314 ¹	2861 2891 ¹	9 9 ¹	5.0
B3G2_R20_B2.5	723 737 ¹	311 317 ¹	2861 2915 ¹	23 23 ¹	5.3

¹True mix design proportions based on the fresh unit weight value (necessary for the mixes where the specific gravity of biochar was not specified)

4.2.2. Influence on fresh mortar properties

The fresh mortar properties results, which are summarized in the table below, showed a similar overall trend as was presented in the previous two subsections of this study. Thus, a low dosage of biochar added into the mortar resulted in a slightly greater dosage of the superplasticizer needed to keep the same flowability of the mortar. It is also worth noting a minor increase in the heat of hydration and a slightly accelerated setting of the mixes with biochar, which can be attributed to the nucleation effect.

Table 4.6. Biochar as an additive in reduced cement mortar - Fresh mortar properties

Mix ID	Flow (%)	SP (fl.oz/ cwt)	Unit Weight (pcf)	Setting time (hrs)		Heat of Hydration (J/g of cement)	
				Initial	Final	24-hr	72-hr
Control	112	-	148	4.7	7.6	208	291
10% cement reduction							
Control-R10%	91 (113*)	2.2	148	4.9	8.2	205	285
B3G2_R10%_B1%	83 (109*)	2.1	149	3.0	6.0	229	
B3G2_R10%_B2.5%	75 (102*)	3.0	148	2.9	6.0	235	
15% cement reduction							
Control-R15%	67 (102*)	3.8	149	5.9	8.8	202	284
B3G2_R15%_B1%	64 (105*)	3.8	147	4.5	7.3	213	286
B3G2_R15%_B2.5%	63 (102*)	4.3	147	4.8	7.2	217	294

20% cement reduction							
Control-R20%	48 (105*)	4.7	148	5.5	8.8	209	291
B3G2_R20%_B1%	51 (109*)	5.0	146	5.0	7.6	217	293
B3G2_R20%_B2.5%	105*	5.3	148	5.3	8.1	214	294

*Flow measured after the application of superplasticizer

4.2.3. Influence on mortar strength

As was mentioned previously, the main goal of this part of the study was to compensate for the decrease in mortar compressive strength associated with cement reduction (shown in Figure 4.5) by introducing a low content of biochar in the mix.

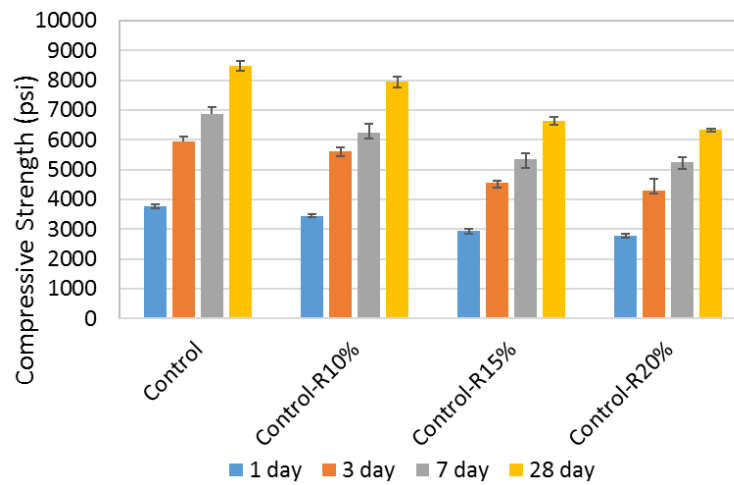
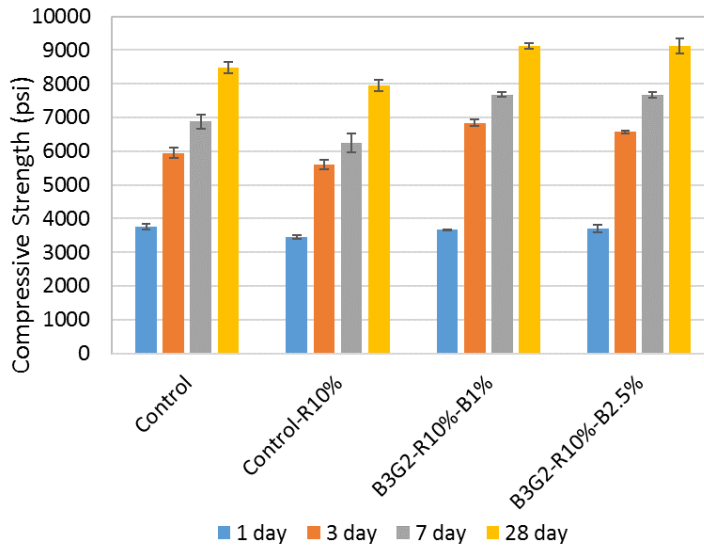


Figure 4.5. Effect of cement reduction on the compressive strength

As can be seen from Figure 4.6, the goal of this part of the study was achieved, as it was possible to not only improve the compressive strength characteristics of the biochar-added mortar (when compared to the corresponding control mixes with the reduced cement content) but to actually recover them to the levels comparable with the original control mix (even for 20% cement reduction).



% Change in f'_c (% change relative to control mix)

#	1d	3d	7d	28d
1	-8	-6	-9	-6
2	-3	+15	+12	+8
3	-1	+10	+11	+8

% Change in f'_c (% change relative to Control-R10%)

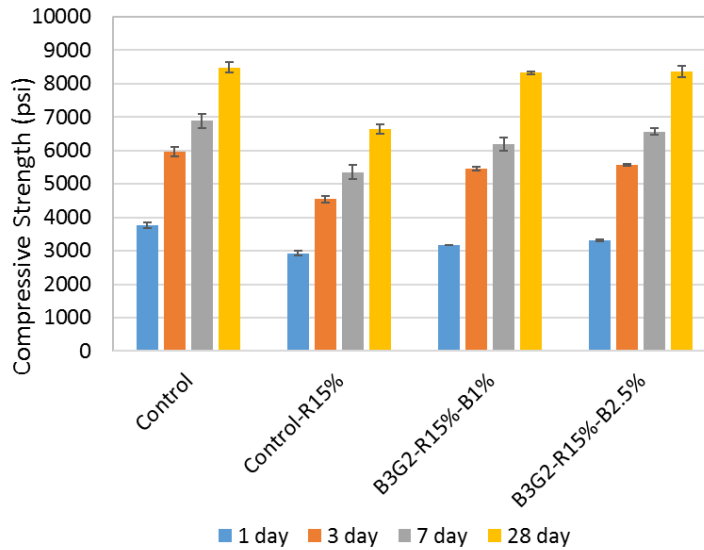
#	1d	3d	7d	28d
2	+6	+22	+23	+15
3	+8	+17	+23	+15

1 – Control-R10%

2 – B3G2-R10%-B1%

3 – B3G2-R10%-B2.5%

a) B3G2 in mortar with 10% cement reduction



% Change in f'_c (% change relative to Control)

#	1d	3d	7d	28d
1	-22	-24	-22	-22
2	-16	-8	-10	-2
3	-12	-6	-5	-1

% Change in f'_c (% change relative to Control-R15%)

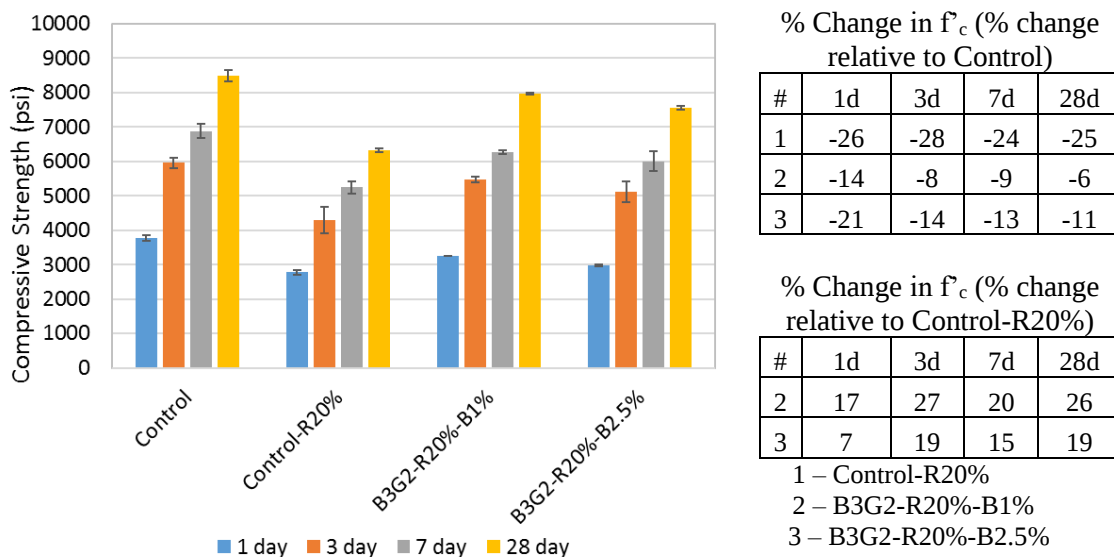
#	1d	3d	7d	28d
2	+8	+20	+16	+25
3	+13	+23	+23	+26

1 – Control-R15%

2 – B3G2-R15%-B1%

3 – B3G2-R15%-B2.5%

b) B3G2 in mortar with 15% cement reduction



c) B3G2 in mortar with 20% cement reduction

Figure 4.6. Biochar as an additive in reduced cement mortar - Effect on compressive strength

4.4. Preliminary study of biochar as an internal curing agent in mortar

Due to its remarkable water absorption properties, it was decided to utilize coarse homogenous biochar sample (B1) as potential internal curing agents. First, biochar was introduced in a wide range of the sand replacement percentage to get a full picture of the effect of the high biochar content on the concrete performance (mix design approach 3). Then, an ultimate approach of taking into account material's absorption and desorption properties was utilized as the second part of this section (mix design approach 4). In addition, a sample of LWFA made from expanded clay was selected as a reference internal agent to be compared with.

The selection of the distillers grain biochar (B1) was also motivated by the fact that it was the only biochar sample, the water absorption and desorption properties of which were possible to measure by means of the test methods described earlier in subsections 3.2.2 and 3.2.3.

Table 4.7. Specific gravity and water absorption/desorption properties of biochar and LWFA

Property	Specific Gravity (SSD)	Water absorption capacity (%)			Water desorption (%) ²
Test Method	ASTM C1761	ASTM C128	ASTM C1761 ¹	Teabag test	ASTM C1761
B1 biochar	1.16	125.9	100.0	100.3	85.7 (85.7)
L1 – LWFA	1.91	-	21.6	-	85.8 (18.5)

¹Used for further calculations

²The value in brackets demonstrates the amount of water being desorbed based on the dry weight of the material

It was decided to proceed with the values measured by means of ASTM C1761 due to the limitations of ASTM C128 (airborne particles formation: resulted in the overestimated value as the test might have been stopped before reaching the SSD condition of particles), and since the teabag test resulted in a very close value (although a portion of biochar particles may escape through the mesh of teabag, which may alter the accuracy).

Nevertheless, it is also worth noting that the results of the teabag test (presented in Figure 4.8) showed that more than 65% of the moisture is being absorbed by biochar in less than a minute and full saturation is reached in less than 24 hours of soaking in water.

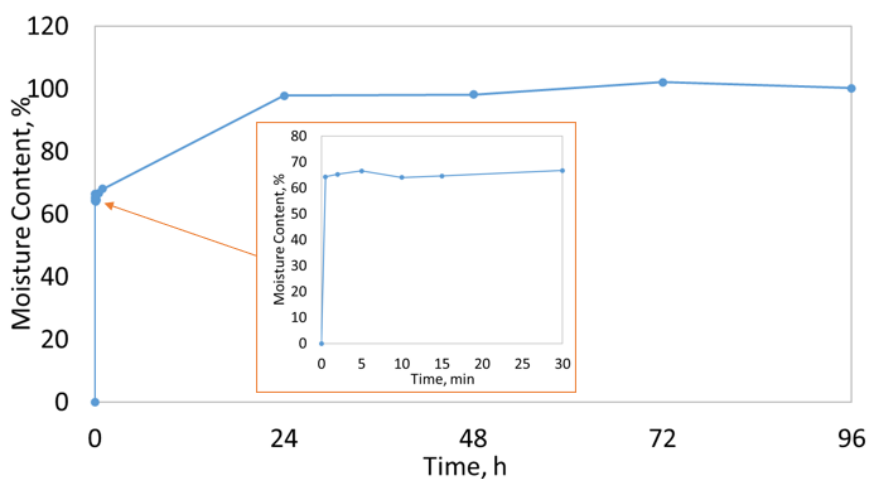


Figure 4.7. Water absorption rate of biochar measured by teabag test

Overall, it can be seen that biochar particles have considerably higher water absorption and desorption capacity values than expanded clay (LWFA), which makes them a suitable candidate for being an internal curing agent.

4.4.1. Mix design approach and proportions

Mix design approach 3 (oven-dry biochar/LWFA as a sand replacement lightweight fine aggregate): the following approach implies the concept of considering the biochar as a lightweight sand replacement substance when the water absorption and specific gravity characteristics of the biochar were taken into account to adjust the amount of mixing water to maintain a constant effective w/c ratio of 0.43. The biochar/LWFA was then premixed and introduced to the mix with the sand.

Mix design approach 4 (pre-soaked biochar/LWFA as an internal curing agent): this method implies the use of biochar or LWFA following the internal curing concept, described in subsection 3.3.1.

Due to its coarse granular structure and fair homogeneity, a sample of as-received distillers grain biochar (B1) was chosen to be the base material for this part of the study. It was decided to explore a wide range of sand replacement percentages (%vol.) and prepare a set of samples to study the effect of high sand replacement amounts.

After that, several selected mixes (B1-IC and L1-IC) were prepared using the optimal dosage of both materials calculated based on the previously introduced equation 4.1.

Table 4.8. Biochar as an internal curing agent - Mix proportions

Mix ID	Cement (pcy)	Water (pcy)	Sand (pcy)	Biochar (pcy)	LWFA (pcy)	Method of curing
Control-W	904	389	2487	-	-	water
Control-V	904	389	2487	-	-	vacuum
B1 – Distillers Grain Biochar						
B1-S10%-W	904	389	2239	109	-	water
B1-S25%-W	904	389	1866	272	-	water
B1-S50%-W	904	389	1244	544	-	water
B1-S75%-W	904	389	622	817	-	water
B1-S100%-W	904	389	-	1089	-	water
B1-S100%-V	904	389	-	1089	-	vacuum
B1-IC-V	904	389	2245	106	-	vacuum
L1 – expanded clay LWFA						
L1-S100%-W	904	389	-	-	1793	water
L1-IC-V	904	389	1803	-	493	vacuum

4.4.2. Influence on fresh mortar properties

As can be seen from the results of the fresh concrete properties (presented in Table 4.9), an introduction of both, biochar and LWFA, in a dry state led to a considerable increase in the workability of the mortar. This might be explained by the fact that not all the water that was expected to be absorbed by the material was actually absorbed immediately, increasing the effective water to cement ratio at the time of mixing and testing the workability. In contrast, the approach of adding pre-soaked materials (B1-IC and L1-IC) resulted in a slight reduction in workability.

Table 4.9. Biochar as an internal curing agent - Fresh mortar properties

Mix ID	Flow (%)	SP (fl.oz/cwt)	Unit Weight (pcf)	Setting time (hrs)		Heat of Hydration (J/g of cement)	
				Initial	Final	24-hr	72-hr
Control	113	-	146	4.8	7.8	200	275
B1 – Distillers Grain Biochar							
B1-S10%	124	-	140	5.3	8.5	211	295
B1-S25%	148	-	131	5.9	9.3	209	291
B1-S50%	143	-	114	6,9	10.2	209	293

B1-S75%	138	-	98	7.6	11.1	218	318
B1-S100%	121	-	83	8.2	11.7	210	309
B1-IC	105	-	142	4.7	7.6	208	288
L1 – expanded clay LWFA							
L1-S100%	156	-	116	4.1	7.8	222	305
L1-IC	98	-	140	4.1	7.2	212	292

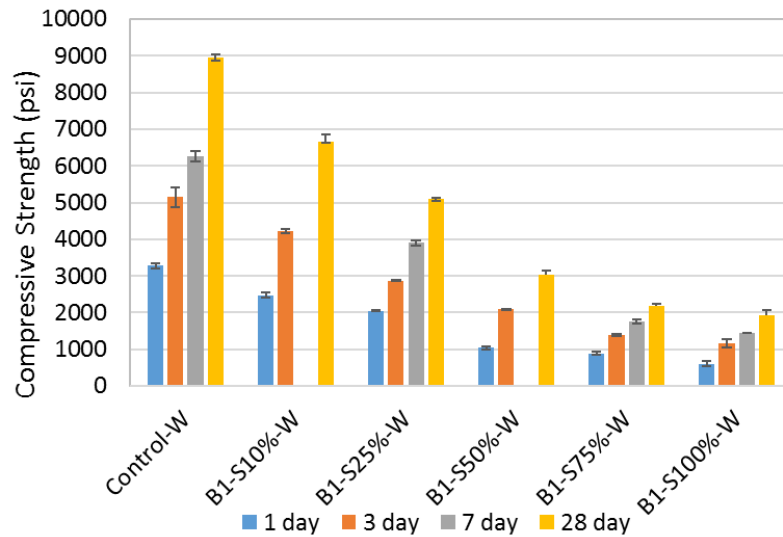
4.4.3. Influence on mortar strength and volume stability

As can be seen from Figure 4.9.a, an increase in the sand replacement percentage with biochar resulted in a significant decrease in the mortar compressive strength, which is in line with the results of the work of Mrad and Chehab (2019), when it was attributed to a porous nature (and subsequently lower mechanical strength) of biochar particles. It is also worth mentioning that even though this approach might not be fully applicable to test the internal curing abilities of biochar (as the water curing does not imply a shortage of water necessary for cement hydration), the results revealed a direct influence of a sand replacement with biochar in the mortar matrix.

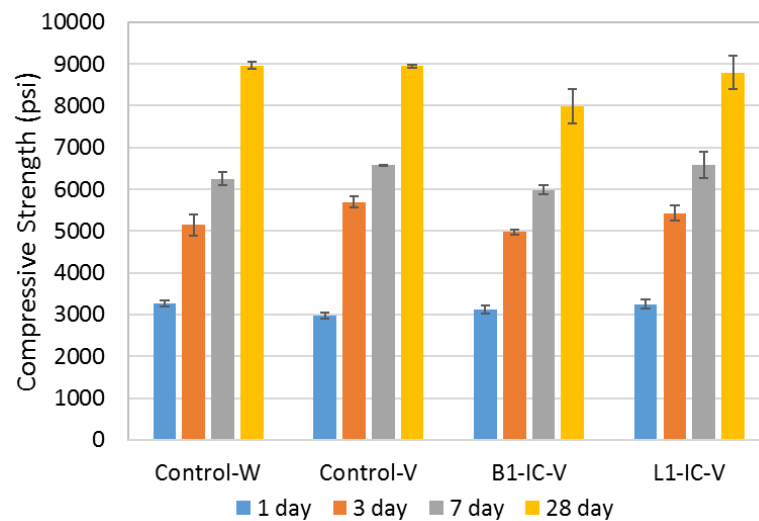
Once the effect of the sand replacement was identified, the internal curing effect of the biochar implementation was assessed by replacing a certain amount of sand (calculated based on biochar's water absorption/desorption properties according to eq. 3.1) and subjecting the specimens to vacuum sealing to avoid external water gain or loss. Thus, the effect of the replacement of sand with biochar for the vacuum-sealed samples is shown in Figure 4.9.b, and, as can be seen, it also resulted in the decrease of the compressive strength.

Moreover, since there was no significant difference between the compressive strength values of the reference mix samples undergoing water and vacuum curing, one may conclude that for the given w/c ratio (0.43) the internal demand in water necessary

for cement hydration is fully satisfied with the initial amount of mixing water and there is no apparent need in internal curing, thus, making the strength drop of B1-IC-V attributable to lower mechanical properties of biochar.



a) Wide range of sand replacement – water curing

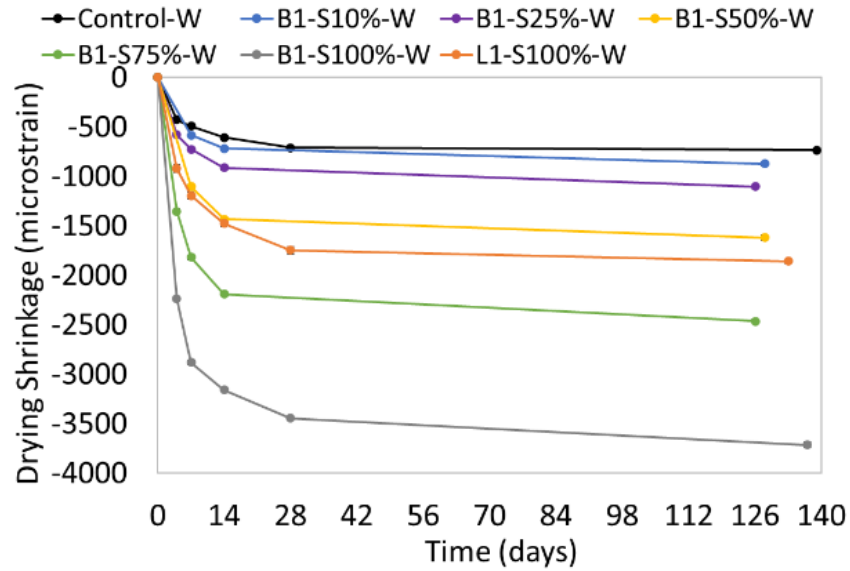


b) Optimal dosage of replacement – vacuum curing

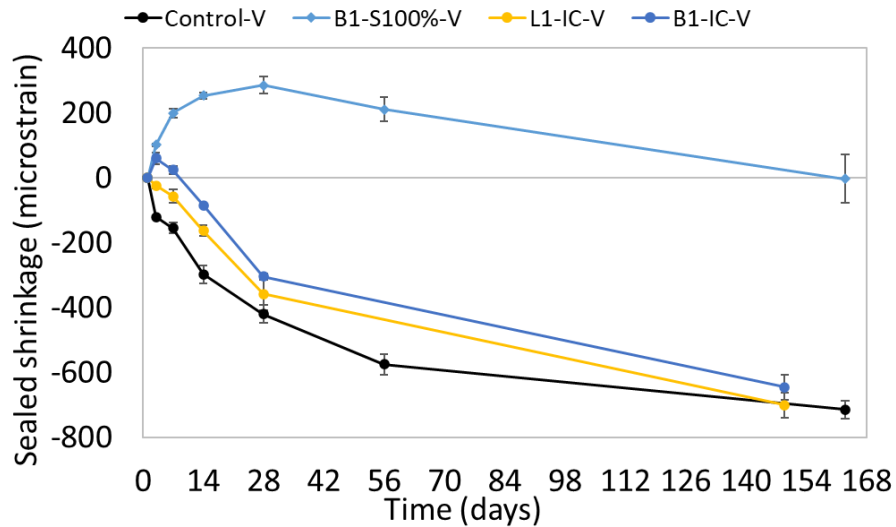
Figure 4.8. Biochar as an internal curing agent - Effect on compressive strength

The effect of the application of biochar on the mortar volume stability is shown in

Figure 4.9.



a) Wide range of sand replacement – drying shrinkage



b) Sealed shrinkage at high and optimum replacement levels

Figure 4.9. Biochar as an internal curing agent - Effect on volume stability

As can be seen, the increase in the sand replacement ratio with biochar and subjecting the specimens to drying resulted in a significant increase in the drying shrinkage value, which can be explained by the additional moisture loss that was stored inside of the porous biochar particles for the samples with higher biochar content. However, a sealed shrinkage testing (Figure 4.9.b) revealed a possibility of decreasing

(and even volume expansion) of the early shrinkage for the covered samples (not subjected to direct drying).

4.5. Preliminary study of biochar to enhance mortar carbonation

The main objectives of this part of the study were to identify if the unique absorption properties of biochar particles could be utilized to promote an improvement in the mechanical strength of the mortar through carbonation initiated internally (introduce CO₂-treated biochar particles in the mix) or externally (possible better retention of CO₂ by biochar particles when mortar blocks are subjected to external CO₂-treatment).

4.5.1. Biochar as an internal carbonation agent

As was mentioned previously, the first approach was to introduce carbonation internally, i.e., assuming that a portion of the CO₂ initially pre-absorbed by biochar will be gradually released in fresh mortar, thereby enhancing the formation of calcium carbonates (mechanically stronger than calcium hydroxide).

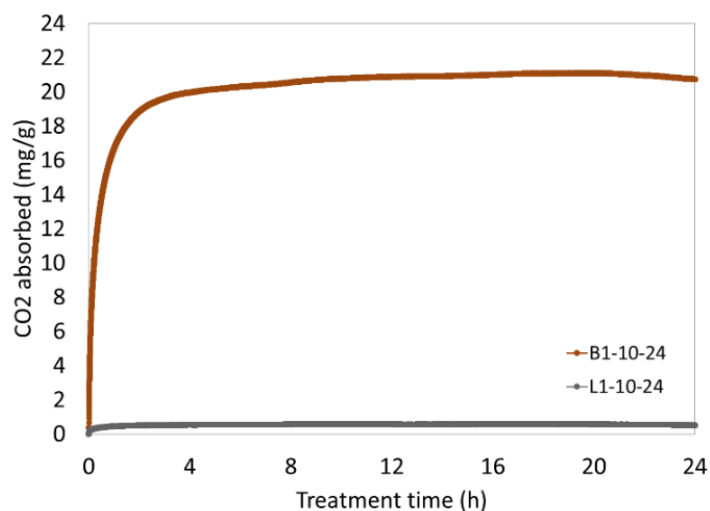
First, it was necessary to study the CO₂ absorption behavior of biochar particles and identify the effect of the main treatment settings: initial gas pressure and treatment duration.

Table 4.10. CO₂ treatment of biochar and LWFA

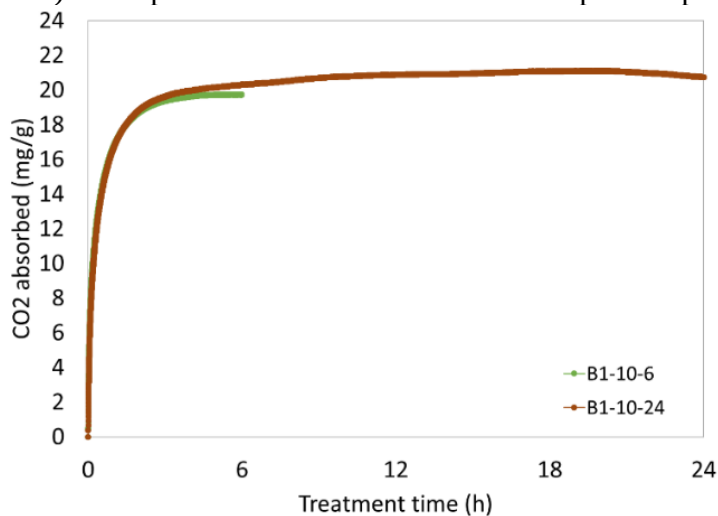
Test ID	Initial pressure (psi)	Treatment duration (hrs)	Sample mass (g)	CO ₂ absorbed (mg/g)	
				Method 1 ¹	Method 2 ²
Biochar treatment					
B1-10-24	10	24	400	53.3	20.6
B1-10-6	10	6	400	47.1	19.7
B1-30-6	30	6	400	56.9	23.1
B1-40-6	40	6	50	61.3	37.7
LWFA treatment					
L1-10-24	10	24	1000	2.3	0.5

¹Method 1 – estimated based on the mass gain (measured before and after the treatment)

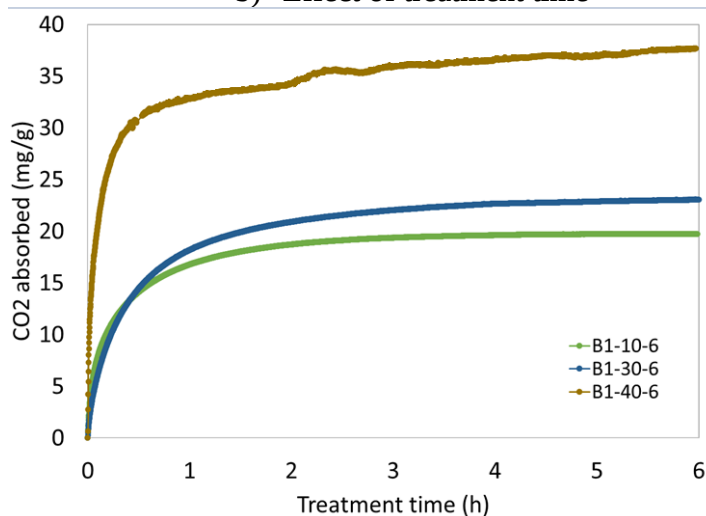
²Method 2 – estimated based on the pressure drop (Van der Waals model)



a) Comparison between B1 and L1 absorption capacities



b) Effect of treatment time



c) Effect of treatment pressure

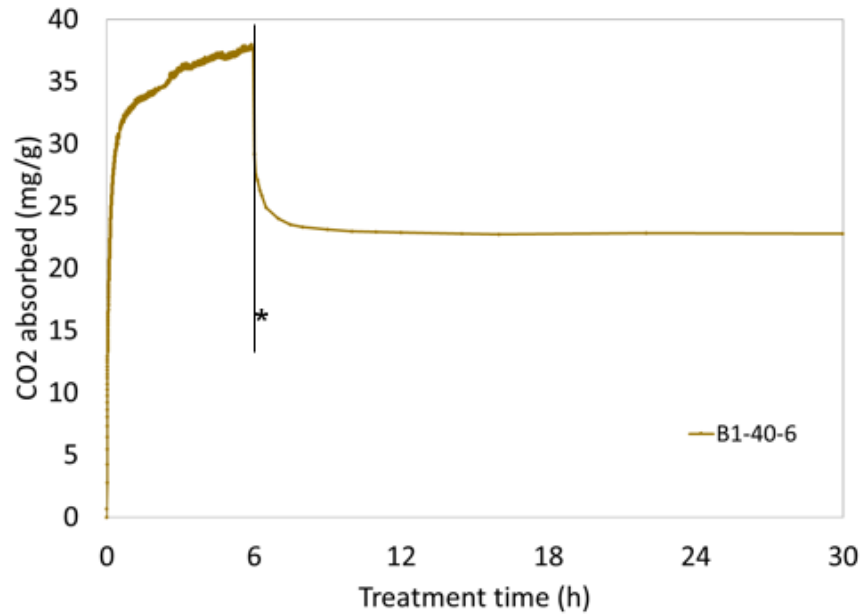
Figure 4.10. Factors affecting the CO₂ absorption process

First of all, the CO₂ absorption characteristics of biochar and lightweight fine aggregate were compared by subjecting an equal amount of both materials (based on bulk volume: 400g and 1000g respectively for B1 and L1) to the treatment of the same conditions: 10 psi of gas pressure for 24 hours. As can be seen from the results shown in Table 4.10 and Figure 4.11.a. the capacity of the biochar to absorb CO₂ is significantly higher than that of the LWFA, which makes it a reasonable candidate for a further application.

Next, the study revealed that extending the treatment up to 24-hr resulted in only a 13% increase in the amount of CO₂ absorbed, and due to time feasibility, it was decided to proceed with a 6-hr treatment for further tests. However, increasing pressure from 10 psi to 30 psi resulted in a 21% increase in CO₂ absorbed, and that is why it was decided to maximize the treatment pressure, reaching the capacity of the setup of 40 psi. Overall, it was decided to proceed with a 40-psi-6-hr treatment for the preparation of the treated biochar samples for a further introduction of them in mortar mix.

Nevertheless, it was also important to estimate the amount of carbon dioxide that was actually absorbed and was not released upon finishing the treatment process (Figure 4.11). Thus, by measuring the amount of the CO₂ released as per the method described previously in section 3.6.3.c, it can be seen that approximately 40% of the originally absorbed CO₂ was released minutes after finishing the treatment process. Although one could state that the remaining portion of 60% is still being retained by biochar particles, it might be possible that some portion of the remaining 60% was desorbed during the pressure release upon finishing the treatment. This could be pointed out as one of the

drawbacks of the introduced test method and might be a subject of modification in future studies.



*Amount of CO₂ being released

Figure 4.11. The rate of CO₂ absorption and release

Nevertheless, immediately after finishing the CO₂-treatment process, biochar samples were introduced in the following set of mixes (Table 4.11), prepared following the mixing approach previously described in subsection 4.1.1.

Table 4.11. Biochar for internal carbonation - Mix proportions

Mix ID	Cement (pcy)	Water (pcy)	Sand (pcy)	Biochar (pcy)	SP (fl.oz/cwt)	Method of Curing
Control-W	904	389	2487	-	-	Water
Control-V	904	389	2487	-	-	Vacuum
B1G1-C5%-V	904	389	2487	45	-	Vacuum
C-B1G1-C5%-V*	904	389	2487	45*	-	Vacuum
B2G1-C10%-W	904	389	2487	90	8	Water
C-B2G1-C10%-W*	904	389	2487	90*	14	Water

*Biochar was subjected to CO₂ treatment at 40 psi pressure for 6 hours and was introduced to the mix immediately after the treatment was finished

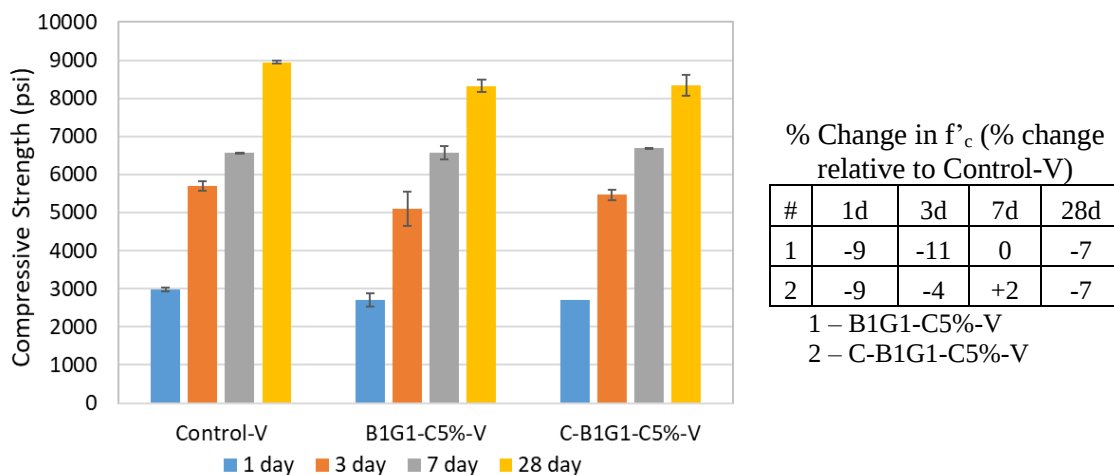
The results (Table 4.12) did not show any significant influence on the fresh mortar properties besides a slight reduction in the flow, which might be associated with a probable release of CO₂ in the mixing water.

Table 4.12. Biochar for internal carbonation - Fresh mortar properties

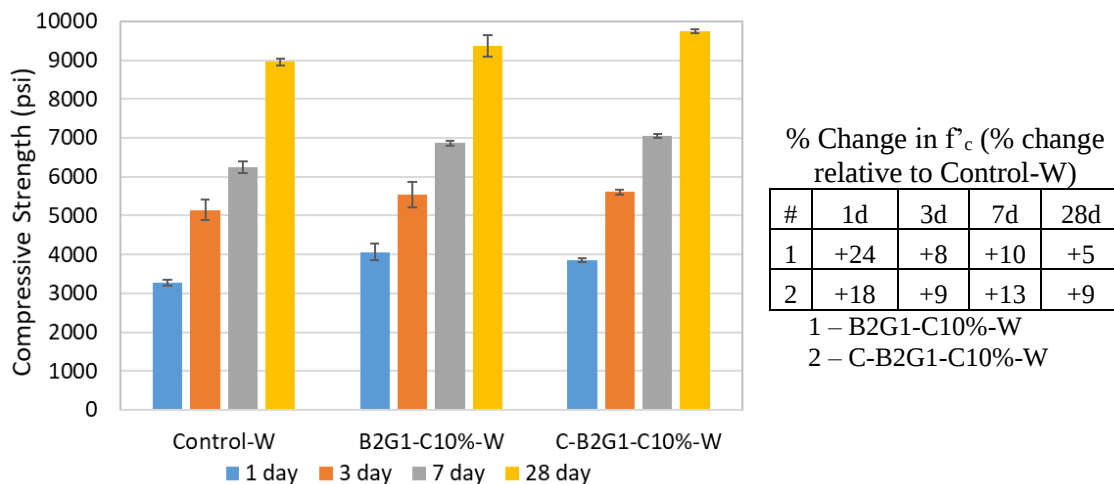
Mix ID	Flow (%)	SP (fl.oz/cwt)	Unit Weight (pcf)	Setting time (hrs)		Heat of Hydration (J/g of cement)	
				Initial	Final	24-hr	72-hr
Control	113	-	146	4.8	7.8	200	275
B1G1-C5%-V	114	-	142	4.6	7.3	203	304
C-B1G1-C5%-V	97	-	142	4.8	8.3	200	313
B2G1-C10%-W	115*	8.0	145	5.8	9.2	224	285
C-B2G1-C10%-W	108*	14.0	145	6.7	9.2	215	286

*Flow measured after the application of superplasticizer

As can be seen from the results of the compressive strength test (Figure 4.12), the addition of both samples of the treated biochar samples did not significantly influence the mechanical strength of mortar, implying that there was little or no effect of the treated biochar particles to promote concrete carbonation.



a) Addition of CO₂-treated B1G1



b) Addition of CO₂-treated B2G1

Figure 4.12. Biochar as an internal carbonation agent - Effect on compressive strength

Moreover, the phenolphthalein was applied on the cross-section of the hardened mortar samples to indicate possible carbonation (Figure 4.13). Initially, the colorless phenolphthalein indicator changes its color to pink when introduced to the basic environment (applicable for normal concrete), and does not change its color when applied on the carbonated concrete surface, associated with a drop of the main basic component of the concrete matrix - calcium hydroxide. Figure 4.14 reveals that there were not any apparent signs of carbonation, meaning that at this stage, either the amount of the absorbed (and stored inside of the pores of biochar) CO₂ was not enough to apply the internal carbonation concept, which is in line with the results of the research study of Wang et al. (2020) (when the addition of the CO₂-treated biochar did not result in the addition carbonation as was shown with the help of TGA) and opposite to the outputs of the study of Gupta et al. (2018). It is also highly possible that a major part of the absorbed CO₂ was released upon the completion of the treatment when the pressure level is reduced back to normal.

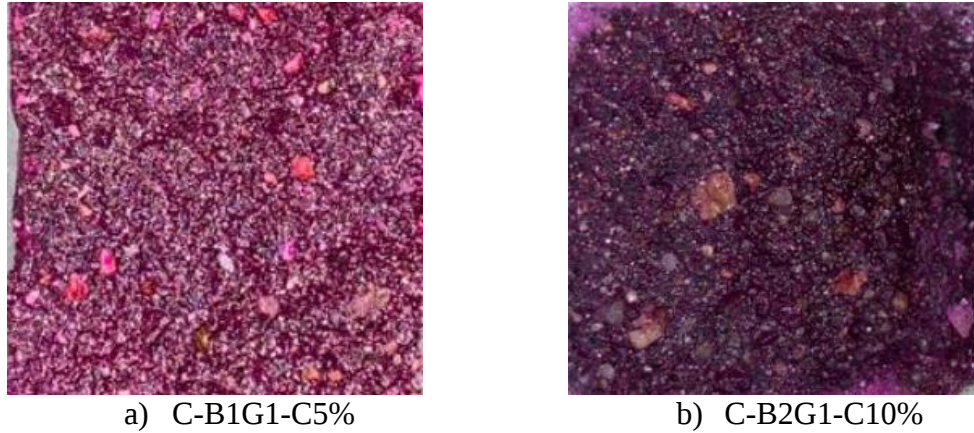


Figure 4.13. Application of the phenolphthalein on the cross-section of the samples

4.5.2. CO₂ treatment of mortar samples with biochar

In the second part of this stage of the study, as an attempt to initiate carbonation of mortar, the following set of mixes were prepared. The biochar incorporation approach and mortar mixing procedure were similar to what was earlier introduced in subsection 4.4.1. However, upon the demolding (24 hours after the mixing procedure was completed), a part of the prepared samples (Control-C and B1-C5%-C) were immediately subjected to the CO₂ treatment according to the procedure described in 3.6.2, while the remaining part was subjected to a vacuum sealing to serve as a reference.

Table 4.13. CO₂ treatment of mortar samples - Mix proportions

Mix ID	Cement (pcy)	Water (pcy)	Sand (pcy)	Biochar (pcy)	Method of curing
Control-V	904	389	2487	-	vacuum
Control-C	904	389	2487	-	carbonation + vacuum
B1-C5%-V	904	389	2487	45	vacuum
B1-C5%-C	904	389	2487	45	carbonation + vacuum

The treatment details are summarized in Table 4.14 and Figure 4.14.

Table 4.14. Concrete specimens CO₂ treatment summary

Test ID	Pressure (psi)	Duration (hrs)	# of samples	Silica gel (g)
Control-C	40	24	10	125
B1-C5%-C	40	24	10	125

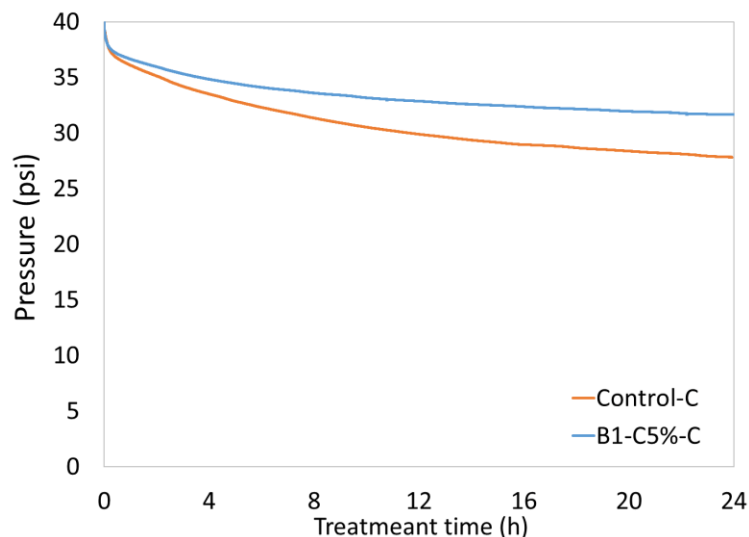


Figure 4.14. CO₂ treatment of 1-day mortar samples

As can be seen from Figure 4.14, there was a bigger CO₂ pressure drop during the treatment of the reference samples when compared to the treatment of B1-C5%-C specimens, which indicates a higher penetration and subsequent absorption of CO₂ gas molecules by plain mortar (the estimated CO₂ absorption values are shown in Table 4.15 and Figure 4.15). This trend is in line with the results of the water absorption properties measurement of the biochar-added mortar performed by previous researchers when lower permeability characteristics of biochar-mortar were attributed to a densified microstructure of the mortar matrix (as a result of high water absorption properties of biochar and subsequent decrease in the effective water to cement ratio) (Gupta et al., 2018a). Although, it is also worth noting that the amount of the CO₂ released upon the completion of the treatment was three times lower for the biochar-incorporated mortar, possibly implying better carbon dioxide retention properties. Nevertheless, it seems like for both of the treatment procedures, there was not enough carbon dioxide absorbed/consumed to reach the full carbonation of the mortar, and a further modification of the approach could be applied in further studies.

Table 4.15. Results of the CO₂ treatment of mortar specimens

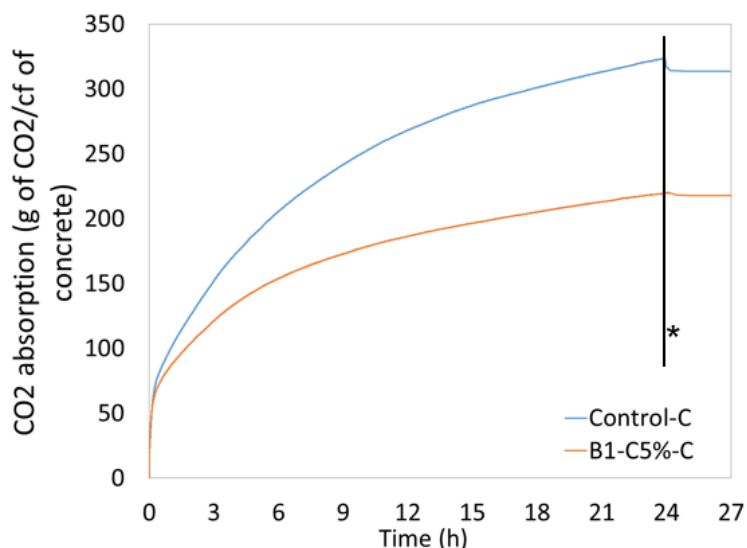
Mix ID	CO ₂ absorbed ¹ (moles of CO ₂ / cf of concrete)	CO ₂ released ² (moles/cf)	CO ₂ released (% of absorbed)	Estimated CO ₂ consumed ³		
				moles/cf	lb/ton	% of complete ⁴
Control-C	7.35	0.22	3.1%	7.13	9.88	7.3%
B1-C5%-C	5.00	0.05	1.1%	4.95	6.86	5.1%

¹The amount of the CO₂ absorbed was calculated based on the gas pressure drop (Figure 4.15) and following the Van der Waals model (subsection 3.6.3.b)

²The amount of the CO₂ released was measured with the method described in subsection 3.6.3.c

³The estimated total amount of the CO₂ absorbed by the mortar specimen was calculated as a difference between absorbed and released values

⁴The estimated amount of the CO₂ required for a complete carbonation of CH contained in 1 ton of concrete – 135 lb of CO₂/ton of concrete



*end of the treatment procedure and the start of the CO₂ desorption test

Figure 4.15. CO₂ absorption and desorption by the treated mortar specimens

Nevertheless, the external carbonation procedure did not significantly influence the mortar mechanical strength characteristics (Figure 4.16) and even revealed a slight reduction in the strength, which possibly indicates that the effect of the carbonation was not enough to overpass a possible moisture loss that might be essential during the first days of cement hydration.

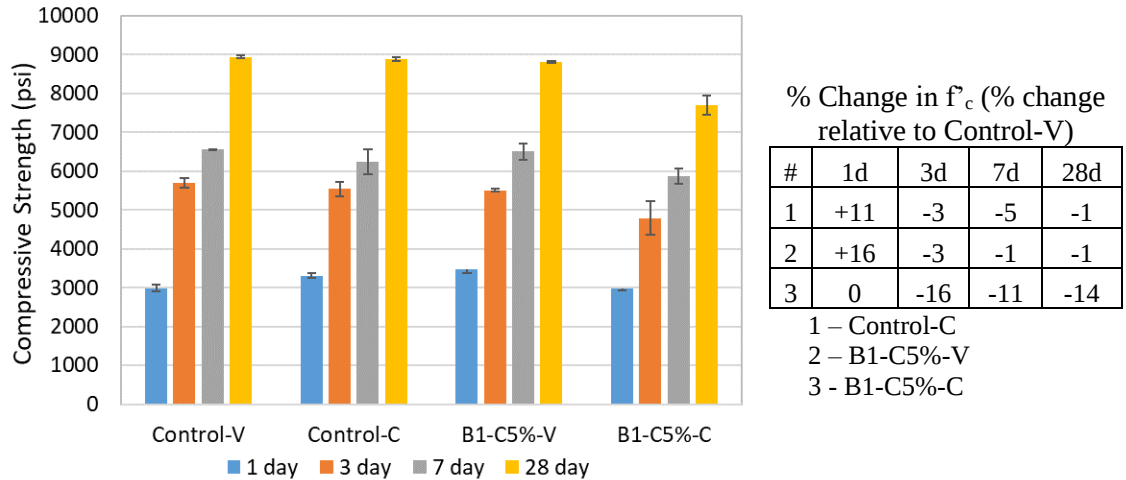


Figure 4.16. Biochar as an additive in reduced cement mortar - Effect on compressive strength

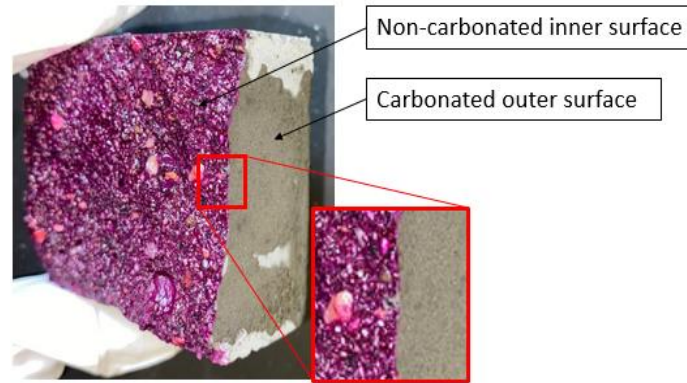
The results of the phenolphthalein application (Figure 4.17.a-b) revealed that the suggested external CO_2 -treatment procedure was not enough to penetrate the mortar matrix, causing carbonation of a thin outer layer of the samples (Figure 4.17.c). This may indicate the necessity of changing the initially suggested external carbonation approach to be applied on the samples with higher initial porosity to let the CO_2 molecules penetrate the mortar matrix.



a) Control-C



b) B1-C5%-C



c) The difference between the inner and outer surfaces of the treated specimen
Figure 4.17. Application of the phenolphthalein on the cross-section of the treated mortar samples

4.6. Biochar as an additive in concrete with RCA

The objective of this part of the project was to study the influence of the biochar application in concrete, and namely an attempt to improve the bonding between recycled concrete aggregates (used as main CA in the set of mixes of this stage) and cement paste, as it was already shown that biochar has a potential to improve ITZ between PP fibers and cement paste (Gupta et al., 2017).

4.6.1. Mix design approach and proportions

Although the biochar implication and the concrete mixing procedure was described in section 3.3.2, it is worth noting that a full attachment of biochar particles on the surface of RCAs was not achieved, as the concrete batch color was darker for all of the biochar-added concrete mixes when compared to the reference mix, indicating a partial dispersion of biochar in the overall concrete matrix.

Nevertheless, it was decided to study the difference between the described two biochar implication approaches (A and B), as well as the effect of biochar content (2.5 and 5.0% of biochar added based on %wt. of cement).

Table 4.16. Biochar as an additive in concrete - Mix proportions

Mix ID	Cement (pcy)	Water (pcy)	RCA (pcy)	FA (pcy)	Biochar (pcy)	WR (fl.oz/cwt)	Biochar addition approach
Control	632	260	1136	1631	-	-	-
B2.5%-A	632	260	1136	1631	16	4.0	A
B2.5%-B	632	260	1136	1631	16	3.0	B
B5.0%-A	632	260	1136	1631	32	8.8	A
B5.0%-B	632	260	1136	1631	32	12.2	B

4.6.2. Influence on fresh concrete properties

The results of fresh concrete properties testing are summarized in the following table:

Table 4.17. Biochar as an additive in concrete - Fresh concrete properties

Mix ID	UW (pcf)	Slump (in)	WR (fl.oz/cwt)
Control	144.1	4.750	0.0
B2.5%-A	144.7	3.750	4.0
B2.5%-B	143.7	3.250	3.0
B5.0%-A	144.2	2.125	8.8
B5.0%-B	145.3	2.250	12.2

As was expected, the addition of biochar resulted in the reduction of the concrete workability, as the demand in water-reducing admixture, used to keep the slump value in the range comparable to the reference mix of target range 2-5 inches, raised with the increase in the biochar dosage introduced in the mix. Similar to the earlier studies of the effect of biochar on mortar workability, this can be explained by the high water retention properties of biochar particles.

4.6.3. Influence on mechanical properties of concrete

Influence on concrete strength

The influence of biochar on the mechanical properties of concrete was assessed by measuring compressive and splitting tensile strength values of biochar-added concrete cylinders and subsequent comparison to the control plain concrete mix.

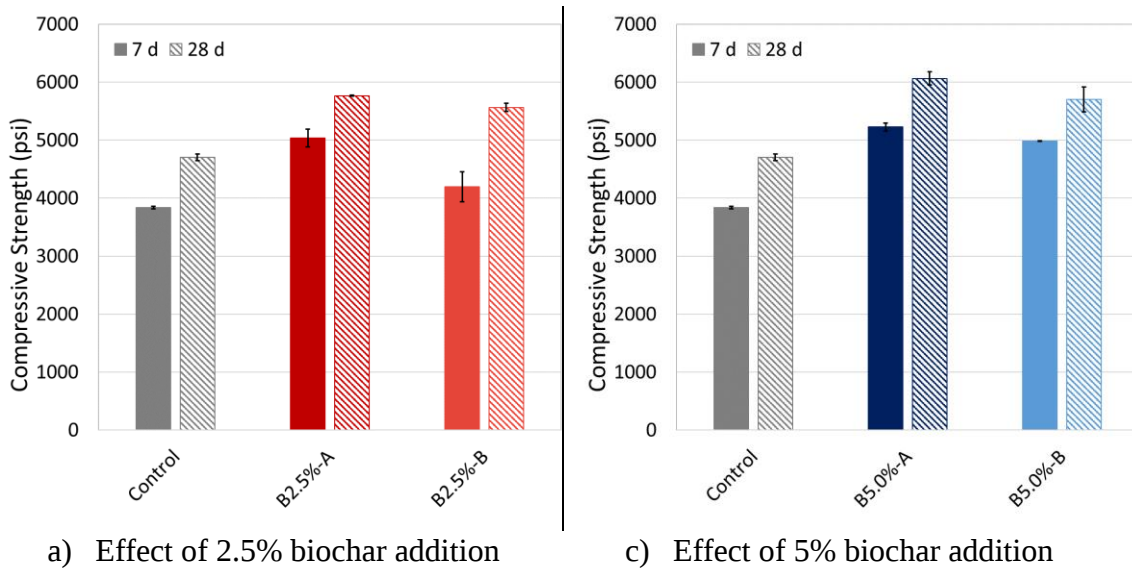


Figure 4.18. Biochar as an additive in concrete – Effect on compressive strength

As can be seen from compressive strength results, the positive effect of biochar application on the compressive strength is increased with higher biochar dosage, which can be attributed to a higher reduction in effective w/c ratio (confirmed by increased demand of the water-reducing admixture applied to maintain the same workability level).

It is also worthwhile to note that the strength increase of the samples prepared through approach B is less noticeable when compared to approach A, which can be explained as follows: although the strength of the paste in the region surrounding the RCAs, as well as the ITZ might be improved, the remaining portion of mortar contains

less amount of cement paste (as a quarter of the original amount was already spent to cover RCAs following the approach B) and thus might be not as strong as specimens from approach A.

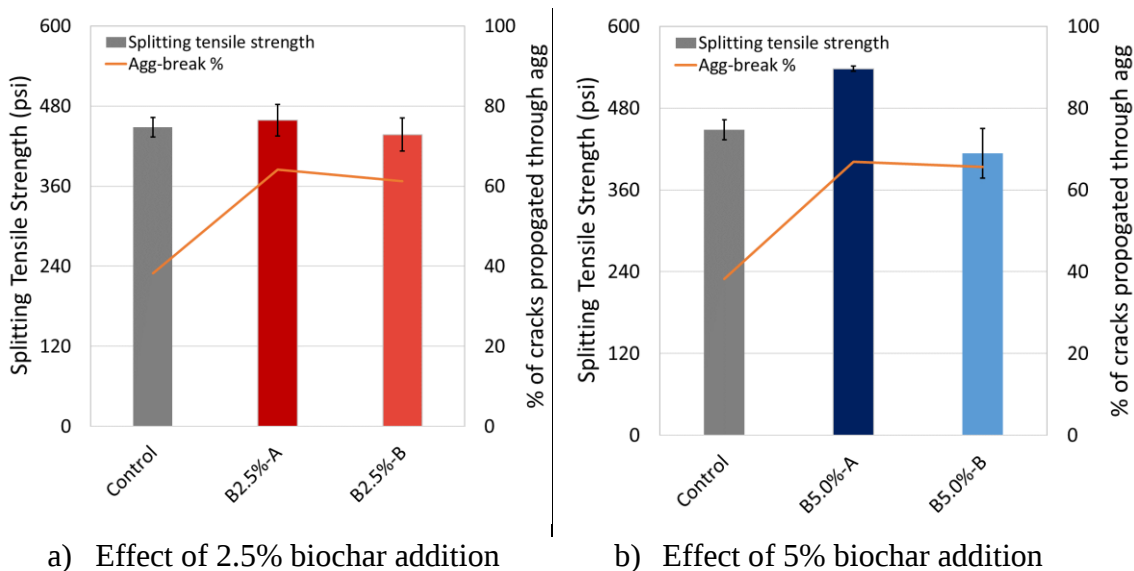


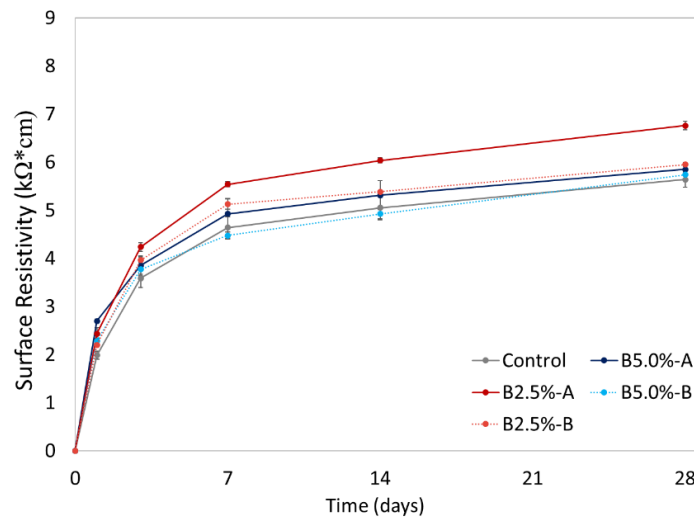
Figure 4.19. Biochar as an additive in concrete – Effect on splitting tensile strength

A similar positive influence of biochar application was observed on the splitting tensile strength results. Again, the effect was significant for the higher dosage of biochar addition, and more apparent for approach A.

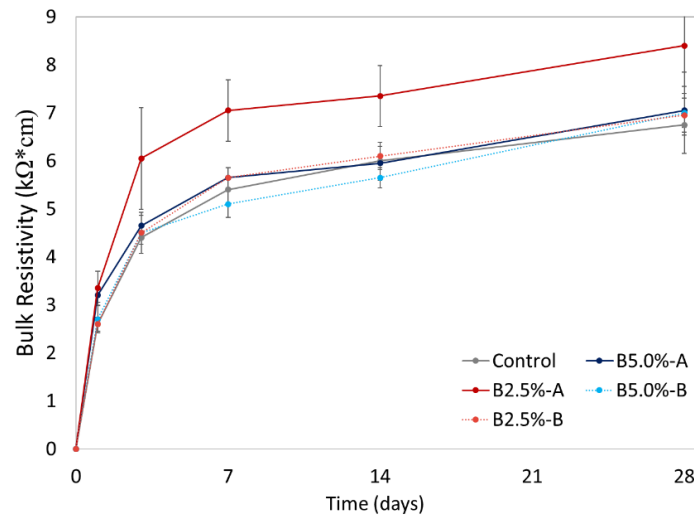
It was also possible to evidence an actual improvement in ITZ by the visual examination of the exposed cross-section of the concrete cylinder broken by splitting tensile test. On average, the percentage of the broken aggregates was higher for biochar-added concrete (64-72%) when compared to the reference plain concrete (38%). Although the higher biochar content ended up with a slightly greater improvement of the value, there was no significant difference between biochar addition approaches (they differ less than 7%), and a more thorough microstructural examination may be required.

Influence on concrete durability

The influence of the biochar addition on the concrete durability properties was evaluated by assessing its resistance to chloride-ion penetration through measuring the electrical resistivity of concrete (Figure 4.20).



a) Effect on surface resistivity



b) Effect on bulk resistivity

Figure 4.20. Biochar as an additive in concrete – Effect on concrete resistivity

As can be seen from the figure above, the addition of biochar resulted in no negative impact on concrete durability, specifically not enhancing mass transport properties of the concrete matrix that may promote chloride ion penetration. This may be

explained by the fact that despite the potential additional porosity of matrix (due to porous nature of biochar particles), the densification of the mortar, which occurred as a result of reduction of effective water-to-cement ratio and a subsequent less amount of capillary pores formed due to additional water absorption and retention by biochar, was a more prevailing factor in the overall mass transport ability of concrete.

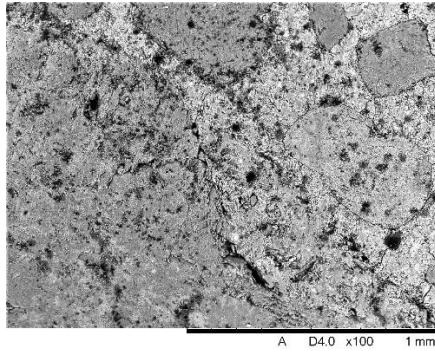
In fact, the positive impact of biochar addition may even be underestimated due to the specificity of the test. As was discussed previously (section 2.4.4), the results of the test might have been affected by enhanced electrical conductivity properties of biochar, and a true effect should possibly be assessed by a more conventional Rapid Chloride Ion Penetration Test and Water Permeability Test.

4.6.4. Visual mortar and ITZ examination using SEM and EDX

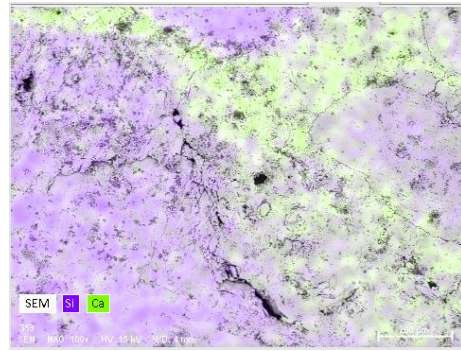
A preliminary visual examination of the selected concrete specimens was conducted in order to support the assumptions derived after analyzing the results from the mechanical strength properties testing described in the previous subsection. The samples for the visual microstructural analysis were obtained from Control, B5.0%-A, and B5.0%-B mixes after 28 days of moist curing.

The visual examination of the microstructure of the obtained specimens conducted using the scanning electron microscope (SEM) was supported with the energy-dispersive X-ray spectroscopy (EDX) in order to accurately identify the boundary region between recycled concrete aggregates (natural aggregates (NA) and old mortar separated by “old” ITZ) and fresh cement paste. The EDX was specifically used for mapping

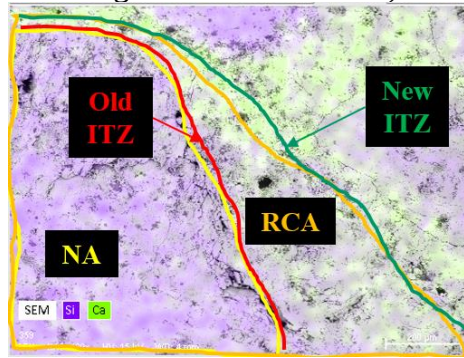
silicon (one of the main elements of most natural aggregates), calcium (the main chemical constituent of cement paste), and carbon (biochar).



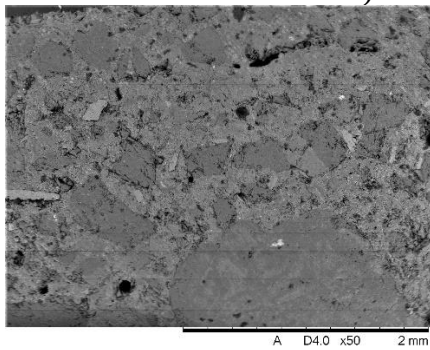
a) Control – SEM image



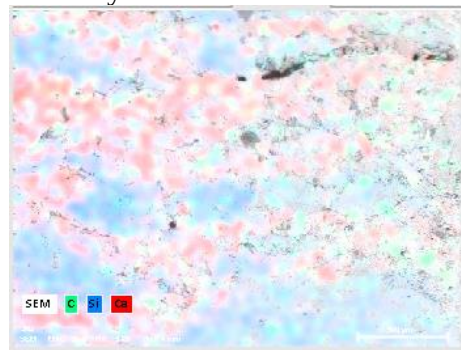
b) Control – EDX mapping



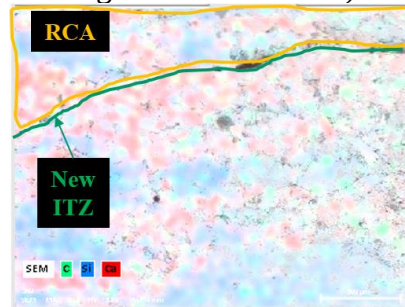
c) Control – visual analysis



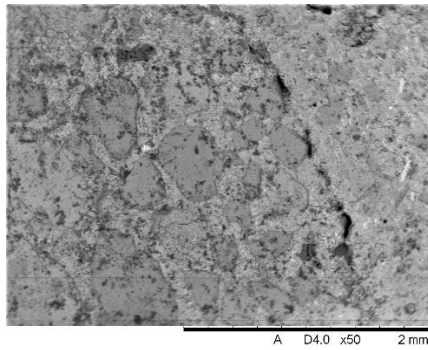
d) B5.0%-A – SEM image



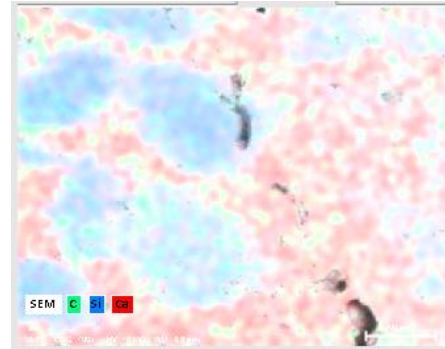
e) B5.0%-A – EDX mapping



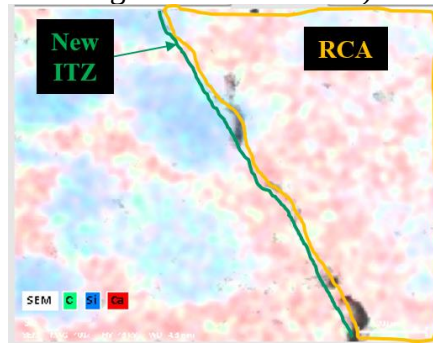
f) B5.0%-A - visual analysis



g) B5.0%-B – SEM image



h) B5.0%-B – EDX mapping



i) B5.0%-B - visual analysis

Figure 4.21. SEM and EDX analysis of the selected specimens

NA – natural aggregate

RCA – recycled concrete aggregate

“Old” ITZ – boundary between NA and old cement paste belonging to RCA

“New” ITZ – boundary region between RCA and cement paste

As was expected, no carbon was identified from the EDX analysis of the control samples (Figure 4.20.a-c), while the signs of high carbon concentration were detected not only along the new ITZ, as biochar particles were initially attached to surfaces of the RCAs, but also outside of that region (Figure 4.20.d-i), supporting the initial assumption that biochar particles were dispersed in fresh mortar surrounding RCAs for both, B5.0%-A and B5.0%-B. Nevertheless, a more thorough microstructural analysis is required (e.g., line-scan to identify the width of ITZ or nano-indentation to directly identify the influence of biochar on mechanical properties of ITZ).

4.7. Statistical analysis

A preliminary statistical analysis was performed to identify the type of the correlation, as well as to estimate which of the biochar characteristics had a statistically more significant influence on the 1-day and 28-days compressive strength of mortar. The analysis was based on the multivariable regression and analysis of variance, and applied for a dataset converged from the selected mortar mixes (51 observations per age), excluding concrete mixes prepared with different design approaches (RCA concrete, internal curing, and carbonation studies).

$$f^c_{c,1d} = 1.946x - 1.514y + 10.997z - 0.0685z^2 + 9.33E-05z^3 - 4E-08z^4 + \text{const. (eq. 4.1)}$$

$$f^c_{c,28d} = 9.880x - 3.412y + 15.164z - 0.09835z^2 + 12.6E-05z^3 - 5.1E-08z^4 + \text{const. (eq. 4.2)}$$

x – Carbon content (%wt.)

y – Biochar particle size (a maximum size of 50% of particles in microns)

z – Biochar content (pcy)

Table 4.18. Type of correlation and level of statistical significance of the observed factors

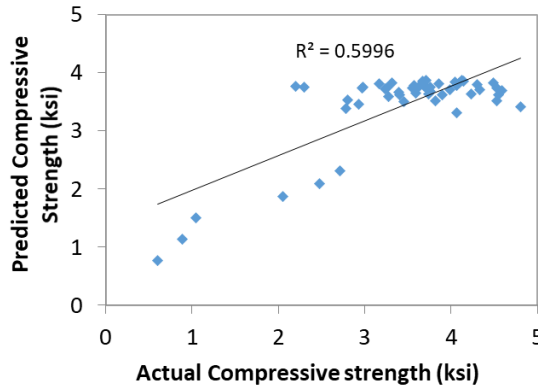
		Biochar type (Carbon content)	Biochar particle size	Biochar content	
Correlation		Linear - positive ¹	Linear – negative ²	Linear - positive	Quartic ³
1d	p-value ⁴	0.193	5.47E-04	0.710	0.0032
28d	p-value ⁴	0.022	3.17E-06	0.987	0.0082

¹A positive linear correlation implies that an increase in the value of the given independent variable results in the increase of the dependent variable value

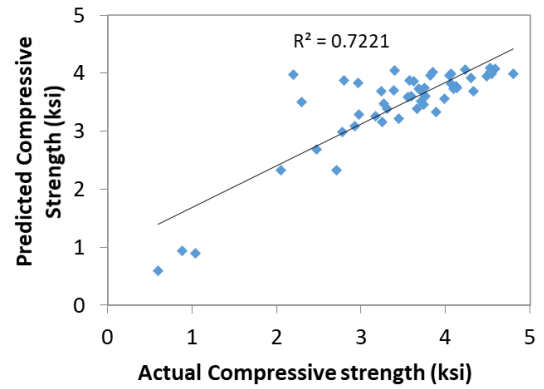
²A negative linear correlation implies that an increase in the value of the given independent variable results in the decrease of the dependent variable value

³Polynomial of 4th degree

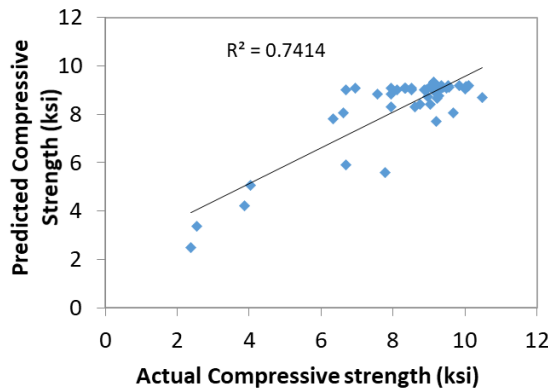
⁴At 95% confidence level p-value should be lower than 0.05 to confirm the statistical significance of the variable



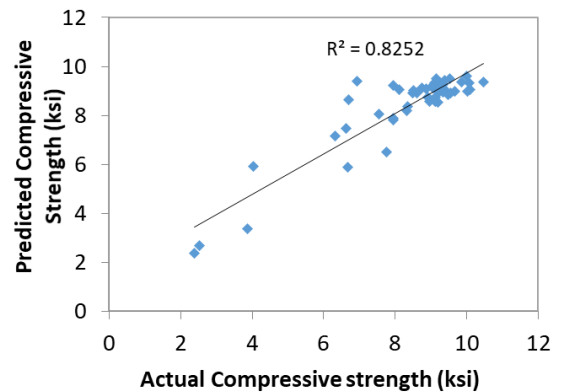
a) 1d – before implying a quartic correlation for biochar content



b) 1d – after implying a quartic correlation for biochar content



c) 28d – before implying a quartic correlation for biochar content



d) 28d – before implying a quartic correlation for biochar content

Figure 4.22. Correlation between the predicted model and actual strength values based on the performed multivariable regression analysis

The initially applied multiple linear regression model resulted in the R-squared values of 0.60 and 0.74 for $f'_{c,1d}$ and $f'_{c,28d}$ respectively, showing that there might be other significant factors affecting the mechanical properties of the mortar (especially for the early age strength development). Nevertheless, the regression model was improved by introducing a polynomial (quartic) relationship between biochar content and mortar strength, resulting in a slightly higher R-squared value of 0.83 (0.72 for early age). Thus, potentially confirming the initial assumption about the effect of biochar content, proposed in section 4.1, when the trend of two peaks of the strength increase was observed for the

wide range of biochar applications. This can potentially be explained by the fact that the increase in biochar content results in mortar strength drop due to less amount of cement per unit volume of concrete and weak mechanical properties of biochar, which is being outbalanced at low dosage (when the introduction of a low amount of weak biochar particles is overtopped by the nucleation effect) and at a higher dosage (when the drop in effective w/c ratio is significant enough to be a more prevailing factor than cement dilution and weak nature of biochar). Although, as the assumption was based on the observations of mixes with B1 and B2, a similarly wide range application might be recommended to be applied for B3 and B4 biochar samples.

Overall, it can be seen that biochar particles size seems to be the most significant factor among the observed three, potentially conforming to the importance of the role of particles size in nucleation and filler effects mechanisms. This correlates with the results shown in the previous subsections when the application of ground biochar resulted in higher mortar strength when compared to original biochar samples regardless of biochar type and mix proportions.

It is also worth mentioning that the biochar type, which was quantified by carbon content, ended up as the least statistically significant factor (even with no significance at 1d), which may indicate that carbon content was not necessarily the best factor to quantify the difference between various biochar samples. This proposes a need for further biochar characterization and considering other factors to serve as quantification factors to analyze the effect of biochar type, such as biochar water absorption capacity and pozzolanic activity (especially for B2 samples, characterized with high silica content. Even though there was not any evidence of noticeably higher heat of hydration or faster

setting, the assumption is made based on the previous work by other researchers – Zeidabadi et al. (2018), where the pozzolanic properties of biochar with relatively high silica content (13%) were experimentally confirmed).

4.8. Cost-effectiveness and feasibility analysis

Taking into account a relatively high unit cost of biochar, a preliminary cost analysis was performed to identify the economic feasibility of introducing biochar in concrete production.

The cost estimation was performed based on the material and transportation cost (both included in unit cost) of local raw materials presented the table 4.19. Note that the unit price of biochar varies depending on the type of feedstock, pre-processing, processing, and post-processing conditions, and was divided into three categories based on the quality of the output product.

Table 4.19. Unit cost of raw materials

Material	Unit cost
Type IP cement	\$135/ton
Limestone	\$25/ton
Sand and Gravel	\$18/ton
Water	\$2.5/ton
Biochar – low quality	\$500/ton
Biochar – medium quality	\$1000/ton
Biochar – high quality	\$1500/ton
Water reducer	\$9/gallon
Air entraining agent	\$7/gallon

A standard 47BD (mixing proportioning for bridge deck construction specified by the Nebraska Department of Transportation) was chosen to be a base mix design for base cost estimation, as well as to modify the mix proportioning with accordance to 10%, 15%

and 20% cement content reduction and addition of 2.5% (based on wt.% of original cement content) of biochar into the mix as follows:

Table 4.20. Mix Proportions for Cost Analysis

Mix ID	Cement (pcy)	Water (pcy)	CA (pcy)	FA (pcy)	Biochar (pcy)	AEA (fl.oz/cwt)	WR (fl.oz/cwt)
47BD	658	250	854	1992	0	1.5	5.0
47BD-R10%- B2.5%	592	225	890	2075	16	1.5	10.0
47BD-R15%- B2.5%	559	213	909	2122	16	1.5	12.5
47BD-R20%- B2.5%	526	200	929	2168	16	1.5	15.0

It is also worthwhile to mention that with raising public awareness of increasing carbon dioxide emission rates and taking into account that the cement production industry is one of the main contributors to that, companies might start being pushed to reduce their CO₂ emissions by compensating their negative environmental impact through various carbon fees. Thus, for example, according to the United States Environmental Protection Agency (2016), the true cost of every ton of carbon dioxide emitted in the atmosphere is \$11-212, representing negative social impact and environmental degradation. It is quite possible that this amount might start being accounted in the price of carbon credit, an asset equivalent of tradable permit/certificate for a company to emit a certain amount of greenhouse gases measured in values of carbon dioxide equivalent amount (tCO₂e). Currently, those carbon offsets might be purchased by sponsoring various projects aimed to contribute to low-carbon development, like energy efficiency or forest management projects. For example, Gold Standard projects offer a price of 1 tCO₂e in a \$9.39-15.07 range. Another approach is to purchase carbon offsets on the voluntary carbon markets, where the latest price was \$3.13 per tCO₂e (Donofrio et al., 2021). The price of one of the

first US-based biochar carbon sink credits supplier, Pacific Biochar, may be as high \$138 per tCO₂e.

According to Portland Concrete Association, the production of one pound of cement results in the emission of 0.9 pounds of CO₂. Along with the mentioned earlier price of carbon offsets on voluntary carbon markets, this ratio was taken into account to calculate a predicted minimum savings (in terms of avoided fees) that concrete producers may get when reducing the amount of cement used in concrete production.

Table 4.21. Projected cost of proposed mixes

Mix ID	Biochar Quality	Base Cost (\$/yd ³)	Carbon savings (\$/yd ³)	Potential Cost (\$/yd ³)
47BD	N/A	60.57	-	60.57
47BD-R10%-B2.5%	Low	62.14	0.19 – 8.20	53.94 - 61.95
	Medium	66.25	0.19 – 8.20	58.05 - 66.06
	High	70.36	0.19 – 8.20	62.16 - 70.18
47BD-R15%-B2.5%	Low	60.71	0.28 – 12.30	48.42 - 60.43
	Medium	64.83	0.28 – 12.30	52.53 - 64.55
	High	68.94	0.28 – 12.30	56.64 - 68.66
47BD-R20%-B2.5%	Low	59.17	0.37 – 16.39	42.77 - 58.80
	Medium	63.28	0.37 – 16.39	46.89 - 62.91
	High	67.39	0.37 – 16.39	51.00 - 67.02

The results of the conducted preliminary cost analysis revealed that economic feasibility was only achieved for the mixes with 15% cement reduction (comparable price) and 20% cement reduction (≈\$1.5 base cost decrease) where the biochar of lowest price (\$500/ton) was used, while other mixes seemed to be more expensive due to despite high unit price of biochar and increased demand in water-reducing admixture.

Although it was possible to predict the potential cost reduction by introducing the concept of carbon credits and the savings associated with it, a more detailed economic analysis should be performed to enhance the feasibility of biochar application.

CHAPTER 5. CONCLUSIONS AND RECOMMENDATION FOR FUTURE STUDIES

5.1. Conclusions

The main goal of this study was to assess if locally available biochar could be used as a beneficial additive in concrete, as well as to promote the environmental and economic benefits of their application. Based on the results of the experimental study, which included a wide range of applications of the collected biochar samples, the following can be concluded:

- Without a significant compromise in workability, a low dosage of biochar (1.0-2.5% based on %wt. of cement) increases the mortar strength in the level sufficient to compensate to the cement content reduction (up to 20%), which can be attributed to nucleation and filler effects.
- High biochar content (up to 15-20%) may considerably increase the early strength of mortar (up to 47% increase depending on the type of biochar) due to a significant reduction in effective water to cement ratio, which also requires extremely high dosage of superplasticizer to maintain the same workability.
- A significant improvement of the mechanical properties of biochar-added RCA concrete mixes was achieved without a noticeable compromise in workability. The positive effect can be explained by mortar strengthening (by dispersed biochar particles) and the improvement of the ITZ between RCAs and cement paste.

- Reducing biochar particles size (through grinding) may enhance the positive effect of biochar application through the increased possibility of nucleation and better particle packing. Also, it appears that biochar fineness is the most statistically significant factor influencing the effect of biochar addition in concrete (when compared to biochar type and content). Thus, biochar grinding should be one of the primary considerations of post-processing changes by biochar producers to improve their final product. However, the process may result in the increase of the production cost and additional CO₂ emissions, which should be taken into account.
- Due to small particle size and high water absorption and desorption properties, biochar can be considered as a promising candidate for the internal curing of mixes with low w/c ratio or samples subjected to harsh curing conditions (e.g., air-curing). In addition, the sealed shrinkage of biochar-added mortar samples decreased, which is attributed to the internal curing effect. However, further study is needed.
- Beneficial carbonation of concrete may be induced by the treatment of biochar or biochar-added concrete with CO₂, utilizing major absorption properties of biochar. However, the approaches used in the preliminary study did not result in complete carbonation, and further study is required.

5.2. Recommendations for future studies

- Further characterization, data collection, and more systematic comparison between different biochar samples might help to analyze which of the biochar characteristics would be most crucial for the mechanical properties enhancement

(e.g., water absorption capacity, surface area, alkalinity, etc.). It might also be beneficial to measure and compare the pozzolanic properties of ordinary high-carbon biochar samples and the samples characterized with relatively high silica content (such as B2).

- Based on the positive results of the low content of biochar to compensate for the reduced cement content in mortar, further research is needed to reduce the amount of cement in currently used concrete mix proportions (e.g., pavement or bridge deck concrete). Moreover, study is needed to evaluate the effect of the cement reduction and biochar addition on the durability properties of concrete, such as shrinkage, chemical resistance, and F/T resistance).
- To achieve a fundamental understanding of the role of biochar in ITZ improvement, a more thorough ITZ examination of the biochar-added concrete might be performed by directly measuring the mechanical properties of the ITZ using nanoindentation.
- Despite the strength drop previously presented in subsection 4.4, the application of pre-soaked biochar as an internal curing agent could still be viable for the mixes where the moisture loss (either external or internal) take place. Thus, the concept might be tested for the samples with a lower w/c ratio or undergoing less favorable curing conditions, such as air-curing.
- A further study is needed to achieve the desired initial penetration of the CO₂ molecules inside the mortar matrix by either altering the mix proportions or initiating the treatment of the specimens at an earlier age before major hardening

occurred to introduce the samples of more permeable microstructure (e.g., treatment of Concrete Masonry Unit)

- Amongst other potential approaches of how biochar might be beneficially used in concrete should be the study of the potential positive impact of biochar on capturing chemicals (especially heavy metals) contained in most of the RCAs (e.g., by means of a leachate test). In addition, a potential use of biochar electrical conductivity properties in the design of conductive concrete (e.g., potentially substituting carbon powder or other expensive constituents) should be explored as well.

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APPENDIX A – BIOCHAR CHARACTERIZATION

A-1. Corn stover biochar (B2) characterization

Table A.1. Corn stover biochar basic properties

Property	Value
Bulk Density	33.5
Organic Carbon	35.4%
Hydrogen/Carbon (H:C)	0.48-0.70
Total Ash	57.1%
Total Nitrogen	0.66%
pH value	11.63
Electrical Conductivity (EC20 w/w)	4.85
Surface Area Correlation	162

A-2. Red cedar biochar (B4) characterization

Table A.2. Red cedar biochar proximate and ultimate analysis results

Component	Wet-Basis Composition	Dry-Basis Composition
Volatile Matter (% w/w)		12.60
Fixed Carbon (% w/w)		71.08
Ash (% w/w)		16.31
Moisture (% w/w)	0.66	0.00
Carbon (% w/w)		74.46
Hydrogen (% w/w)		1.32
Nitrogen (% w/w)		0.34
Oxygen (dff) (% w/w)		7.55
Sulfur (% w/w)		0.02
Chlorine (µg/g)		111
HHV (Btu/lb)		11,381